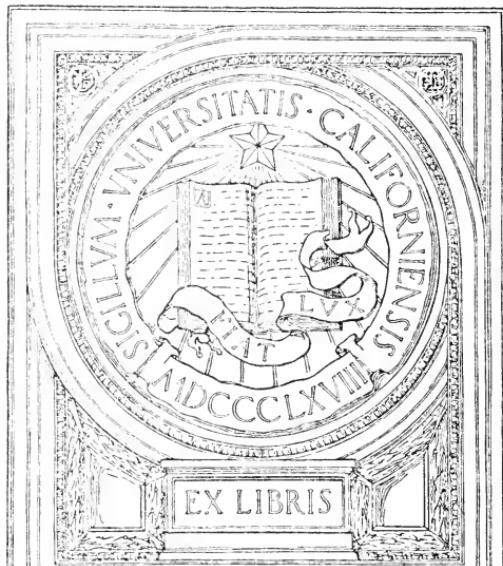


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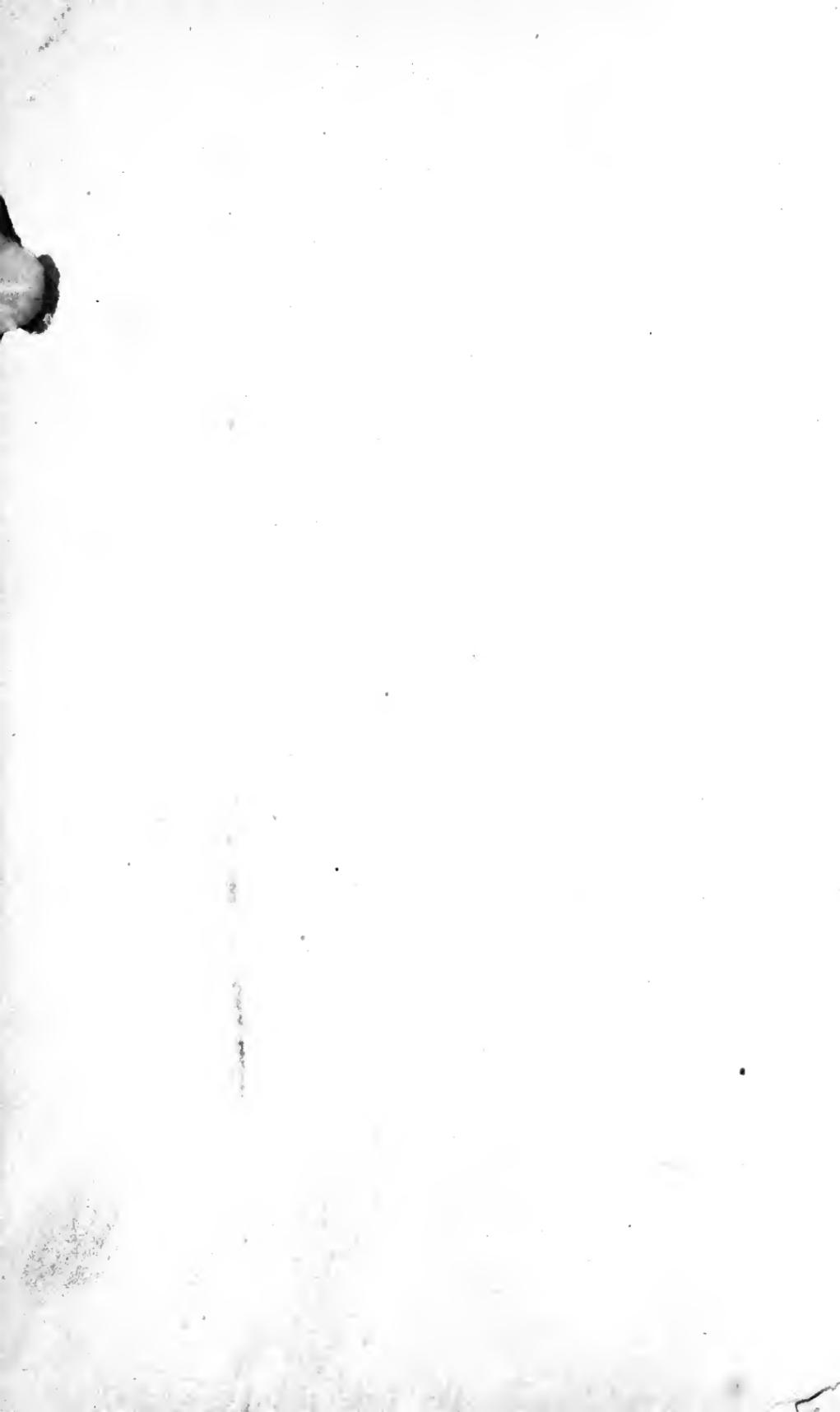


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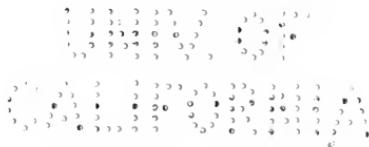


# FIRST PRINCIPLES OF CHEMICAL THEORY

BY

C. H. MATHEWSON, PH.D.

INSTRUCTOR IN CHEMISTRY AND METALLOGRAPHY AT THE  
SHEFFIELD SCIENTIFIC SCHOOL OF  
YALE UNIVERSITY



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## PREFACE.

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THIS small volume has been prepared for the use of first year students at the Sheffield Scientific School, as reference text in connection with a short course of lectures on Chemical Theory. A period of six weeks immediately following the first four months' instruction in General Chemistry is devoted to work of this nature. General principles and theoretical topics are discussed with the utmost simplicity, and in particular view of their continued application. During this time recitations and laboratory exercises are adjusted to the particular task of explaining and emphasizing the lecture subjects.

It is not the intention to segregate and summarily dispose of much important material by untimely or unduly restricted discussion under the above heading. The purpose is rather to offer very early presentation of leading principles which are of material assistance in teaching the beginner to properly explain and correlate his experimental results. Such preliminary preparation permits very open class room discussion of the specific chemical phenomena, which are gradually developed in the laboratory. Every opportunity for illustrating and applying these principles is improved as the actual chemical experience of the student increases.

The advisability of using the Electrolytic Dissociation Theory and the Mass Action Law in first year work is no longer questioned by most teachers. It is rather a question of when and how these subjects should be introduced. As soon as the student has acquired practical familiarity with the molecular and atomic theory and is able to fully comprehend a few of the more general types of chemical change, no particular difficulty will be met in studying the characteristic behavior of electrolytes in aqueous solution, or the effect of enforced concentration changes (formation of gaseous or insoluble products) on the course of a reaction.

A fair measure of success has been attained at the Sheffield Scientific School in the early introduction of these subjects along most general lines, preceded by a few months' introductory work and supplemented by continual repetition and illustration in the class room, as additional chemical facts accumulate.

Before beginning this course, the student should be able to read the introductory chapter with intelligence and a consciousness of familiarity with most of the included material. Incidental remarks on the Kinetic Theory are intended mainly as an aid in picturing a helpful constructive view of matter and more forcibly defining the different states of aggregation.

The brief discussion of the Periodic System (Chapter II) is also of a preliminary nature. Familiarity with the halogen group alone is assumed. Since the elements are invariably presented for study in some sequence based on the natural classification, an elementary exposition of this arrangement seems desirable at the outset. More detailed consideration of this subject (if, indeed, at all necessary) must be deferred until a large number of elements have been studied.

Doubtless too little time is available in most elementary courses for any other than cursory consideration of the principles governing equilibrium in heterogeneous mixtures. The fundamental condition that stable contact of different phases must correspond to definitely fixed values of pressure, temperature, and concentration, seems, however, well worth some attention. Brief discussion of the pressure-temperature diagram in a one-component system may at least be offered with propriety, and any thoughtful student cannot fail to welcome the better understanding of sublimation, vapor pressure, critical temperature, allotropic modifications, etc., which is sure to result from a well ordered effort in this direction. Discriminative application of the Phase Rule adds to the effectiveness of the general discussion.

It may be urged that any text which offers a condensed treatment of leading topics, is read by the student with a considerable show of enthusiasm. There is a greater tendency to grasp the essentials of important material appearing consecutively on a few pages, than to locate and assimilate the same information by perusing the mass of material between the covers of some large

book. College teachers who have adopted a similar plan of introducing these topics, may find this little volume of assistance in connection with some one of the general treatises on Inorganic Chemistry, available at the present time.

For assistance in the preparation of these notes, the author is indebted to Professor Percy T. Walden, who has offered many suggestions emanating from a valuable teaching experience; to Dr. Carl O. Johns, an associate in first year instruction; and to Professor William G. Mixter, under whose active direction this course has been presented at the Sheffield Scientific School.

C. H. MATHEWSON.

JUNE, 1908.



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# FIRST PRINCIPLES OF CHEMICAL THEORY

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## CHAPTER I.

### *INTRODUCTION.*

#### OUTLINE OF LEADING PRINCIPLES AND COMMON CONVENTIONS PERTAINING TO THE STUDY OF GENERAL INORGANIC CHEMISTRY.

THE most casual observer recognizes great diversity in the nature and form of material objects. Natural transformations of matter as the result of varying terrestrial conditions, are phenomena of frequent occurrence. We learn at the outset to distinguish between three common forms in which matter appears, namely, solid, liquid, and gaseous and to realize the potency of certain influences to render these different states interchangeable. Thus, the effect of heating, or adding heat to liquid water is to convert it into water vapor and the effect of adequately cooling, or abstracting heat from liquid water is to produce the solid material called ice. Throughout the course of such transformation, this particular variety of matter, water, has retained its integral composition; it has merely suffered change in its manner of physical appearance. Such alteration is termed **physical change**.

The corrosive action of moist air on many metals constitutes a type of alteration in the matter concerned, which produces results of a far more radical nature. The following specific case serves adequately by way of illustration. If the metal sodium is dropped into water, violent agitation begins immediately. An inflammable gas is liberated, heat is evolved and the metal melts and moves rapidly about on the surface of the water, eventually disappearing. In place of the original group, or

collection of matter consisting of sodium and water, we have, at the close of the transformation, an entirely new system composed of the gas hydrogen (a primary constituent of water), and a substance known as sodium hydroxide (consisting, in part, of sodium and, in part, of elementary particles from water), dissolved in the unchanged remainder, or **excess**, of water. A deep seated process of this sort affecting the individuality, or ultimate chemical composition of the matter involved, is termed a **chemical reaction**. The alteration which matter sustains, as the result of such reaction, is termed **chemical change**.

Aside from the material changes affecting substances concerned in chemical reaction, additional changes of an equally fundamental character invariably accompany such transformation. These changes are intimately associated with the obvious change in the nature of the materials themselves, and are discussed under the general heading of **energy**. The relation of energy to matter exercises a most subtle influence over all physical and chemical phenomena. Extended consideration of this subject is fruitful only to those far advanced in the study of both Chemistry and Physics. It is, however, essential, in this connection, to emphasize the general principle that energy associates itself with matter, supplying the inherent capability for transformation and the performance of work, which all matter possesses.

We recognize the existence of different forms of energy generally susceptible to inter-transformation. The copper wire, which transports electrical energy, becomes warm from the continuous change of electrical into heat energy. In the motor, electrical energy is converted into mechanical energy, some of which is, in turn, changed into heat energy by friction of the bearing parts. During the course of a chemical reaction we frequently observe that **chemical energy**, or energy stored within chemical substances, appears as heat. Other energy manifestations and transformations are familiar to the student of physics.

The form, or **state of aggregation** in which a pure substance exists, depends upon the amount of energy which it possesses. For example, the metal copper, in its ordinary solid state, contains less energy than when in the molten state. Addition

of heat to the solid metal first causes a rise in temperature. When a definite temperature, called the *melting point*, is reached, further heat addition fails to elevate the temperature, but is absorbed in effecting change from the solid to the liquid state. The analogous change from the liquid to the gaseous state takes place when heat is added at a characteristic temperature, called the *boiling point*.

Evidence which has accrued from several centuries of experimental work, and which has become more accurate and convincing with the progressive refinement of methods and skill in manipulation, leads consistently to the conclusion that matter and energy, although capable of great variety of change, cannot be created or destroyed. These two all-important principles are known as **conservation of matter** and **conservation of energy**.

By means of properly ordered chemical operations, composite matter may be resolved into its simplest forms. In this manner, some 80 forms of matter are recognized at the present day as **elements**, or elementary substances incapable of further decomposition. Any other form of matter, which retains its integral nature after being subjected to a variety of physical processes tending to isolate it from other associated substances, is complex, containing two or more of these elements in such intimate union that they have apparently lost all physical individuality. Such substances are called **chemical compounds** and their elementary constituents are said to be **chemically combined**. The general properties of a chemical compound are thus quite different from those of its constituent elements.

The characteristic of greatest importance in establishing the individuality of a chemical compound, is the **constancy of its composition**. *A given chemical compound, whatever its origin, or state of aggregation, invariably contains the same elements in the same proportions.* This epoch-making generalization, known as the **law of constant composition**, or the **law of definite proportions**, rests on a most satisfactory experimental basis. The possible variation in the composition of certain compounds which have been exhaustively investigated, cannot exceed one part in a million by weight. Hence, the above statement becomes an axiomatic fact as far as human agency can determine.

While the law of constant composition certifies to the impossi-

bility of variation in the composition of a chemical compound, it is a matter of common experience that the same elements may occur combined in more than one definite proportion by weight. In such a case, several individual compounds exist, each conforming to the general law. Closer study of these relations has revealed the following important generalization, known as the **law of multiple proportions**, which serves to further characterize the combining habits of the elements. *When two elements unite to form more than one chemical compound, the different weights of one element, which combine with one and the same weight of the other element, stand to one another in the ratio of simple integers.* For example, the five known compounds containing only oxygen and nitrogen, have been shown to possess the percentage compositions, by weight, indicated by the accompanying figures:

	Nitrogen.	Oxygen.		
Nitrous oxide.....	63.65	36.35	0.57	1
Nitric oxide.....	46.69	53.31	1.14	2
Nitrogen dioxide.....	36.86	63.14	1.71	3
Nitrogen trioxide.....	30.45	69.55	2.28	4
Nitrogen pentoxide.....	25.94	74.06	2.85	5

Different weights of oxygen which may combine with one part, by weight, of nitrogen, are given in the third column of figures. It is observed that these numbers are directly proportional to the simple integers in the next column.

A number of pure chemical compounds may be physically intermixed to an extent dependent on their specific properties and states of aggregation. All gaseous materials are completely *miscible*, producing a most intimate type of **physical mixture**. Liquids exhibit all degrees of *miscibility*, or mutual solubility. Immiscible liquids may be mechanically converted into an *emulsion* by agitation. Solids may also attain a very intimate state of mutual incorporation, particularly when obtained from a molten liquid mixture by abstraction of heat. The term, *solid solution*, is used in this connection. In all the above cases, certain physical operations may be devised and used for separation of the co-existent substances.

The conception that diverse physical and chemical processes may not bring about an infinite division of matter, but that certain finite limits in the masses of the ultimate particles are arbitrarily imposed, had proved attractive to philosophers long before Chemistry had attained the standing of an exact science. The development of earlier ideas which presents a satisfactory conception of material transformations accompanying physical and chemical processes, embodies three finite stages in the ultimate division of matter. The first division does not alter the chemical nature of the material and may be accomplished by physical agency. More specifically, in terms of the **molecular theory of matter**, *any material, whether of an elementary or compound nature, is composed of a number of finite particles, called molecules, alike among themselves and assembled in certain well defined states of aggregation.* We have here, as a further development, the characterization of each different physical aggregation of particles by an essential complement of physical properties. Thus, solids, which constitute the most compact form of matter — consisting of closely aggregated molecules — are rigid and not easily penetrable. In an **amorphous**, or **non-crystalline** solid, the closely packed molecules present no regular order of arrangement; hence, the material possesses identical properties in all directions, or is *isotropic*. A **crystalline** solid possesses directional properties, i.e., it is *anisotropic*, owing to the arrangement of its molecules in definite planes of symmetry. The molecules of a liquid are less restricted in their sphere of activity and may easily be displaced; hence, great mobility: while those of a gas are widely separated (maximum volume) and prone to fly apart without restriction.

Beyond this molecular division of matter there is recognized, according to the **atomic theory of matter**, *an arrangement of more elementary particles, called atoms, which may be modified only by processes which we term chemical.* Each different kind of atom represents one of the 80 or more elementary substances. Atoms of the same kind are identical, each variety possessing as especial characteristics, *definite mass and a certain specific tendency to combine with others of the same kind to form the molecules which constitute, in their aggregate, the physical*

material of this specific variety, and *with atoms of other kinds* to form the molecules of various chemical compounds.

Finally, convincing evidence of disintegration of atoms themselves has accumulated during the past ten or a dozen years. Sub-atomic particles invariably carry electric charges and have been called **corpuscles**. Atoms of certain kinds (radium, thorium atoms, etc.) disintegrate spontaneously, forming a series of intermediate "atoms" or arrangements of corpuscles, which possess varying stability and continue to break down with greater or less rapidity, forming others, etc. The existence of negative corpuscles, so small that approximately a thousand of them would be required to make up the mass of the hydrogen atom, has been clearly demonstrated. Much investigation bearing on the development of the **corpuscular theory of matter** is in progress at the present time. While results of a fundamental character have already attended experimental effort in this direction, it should be made evident to the student of Chemistry that no increased perception of chemical phenomena has followed in the wake of these new ideas: the *atom* still remains the unit of chemical change, and the above mentioned disintegration phenomena constitute an order of alteration in matter entirely apart from that which we shall consider in the following pages.

\* Two classes of phenomena, that accompanying the electric discharge through gases and that associated with so-called radio-active bodies, have constituted the experimental basis for the development of the corpuscular theory. Detailed consideration of intricate physical problems which have arisen in connection with the interpretation of such phenomena is entirely beyond the scope of this text. Nevertheless, in deference to a widespread interest in the unique and startling results which have marked this class of investigation, a brief statement of some generally accepted conclusions may be added at this point. It is not presumed that the student will gain an adequate appreciation of this essentially difficult subject at this juncture, but merely that some better conception of these ideas, in which he may already have acquired a general interest, may result from a reading of the ensuing remarks.

An enormous electrical force (potential difference) is necessary to cause a visible discharge to pass through a short space enclosing any gas under ordinary pressure. If the pressure of the gas is greatly diminished the discharge passes much more readily. At extremely low pressures a greater potential difference is again required. Very ordinary electrical apparatus, however,—an influence electric machine, or a voltaic battery in connection with an induc-

\* The author is indebted to Dr. Boltwood for certain criticisms on this part of the manuscript.

tion coil — is capable of supplying electrical energy in satisfactory form and quantity for this purpose. For experiments of this sort, partially evacuated glass tubes with sealed-in metallic conductors (electrodes) are generally used. Under properly regulated conditions of gaseous and electrical pressure, the discharge presents features of unusual interest. First of importance in this connection is the production of cathode rays within the vacuum tube. Secondary phenomena which are generally attributed to the action of the cathode rays are (1) a characteristic green fluorescence on the anode and the glass opposite the cathode — the space in the vicinity of the cathode remaining dark — and (2) the Roentgen ray effects.

The cathode rays are now conceded to consist in rapid flights of negatively charged particles in straight lines directly away from the cathode or negative pole. Many experiments have been devised to prove that this conception is a true one. For example, suitably mounted mica vanes will rotate if placed in the path of the rays. Moreover, by giving that surface of the cathode which is opposite the anode, the proper degree of concavity, the moving particles may be uniformly directed against an anode of small dimensions. In this way the energy of the moving particles is concentrated to such an extent that anodes of the most refractory metals may be fused. Again, cathode rays may be deflected by the application of electrical or magnetic forces, as any stream of charged particles would be.

Elaborate investigation has shown that these particles, called corpuscles or electrons, may possess a velocity under the most favorable conditions one-third as great as that of light (i.e., they may move at the rate of some 60,000 miles per second), that their individual mass is from one to two-thousandths that of the hydrogen atom and that this mass is invariably the same whatever the gas used in the tube, or the material from which the electrodes are constructed. We believe them, in effect, to constitute the ultimate particles from which all matter is constructed. [The deflection of the charged particles — observed directly by the change in position of a spot of fluorescent light caused by their impacts upon a screen coated with a suitable material — under the influence of a given electrical force is related to both the velocity of the particles and the ratio of the mass of a particle to the charge which it carries, through a known equation. The same quantities constitute the unknown values in an equation defining the deflection in a magnetic instead of an electrical field. Thus, the two quantities are completely defined through two sets of experiments. Velocities of  $2 - 3 \times 10^9$  cm/sec. are commonly observed in these experiments (that of light is  $3 \times 10^{10}$  cm/sec.) The second quantity, which appears as a ratio, is always constant. Several methods have been used with concordant results in fixing the magnitude of the charge carried by a corpuscle (one term of the ratio). This value is also invariably constant and is identical with the charge carried by certain atoms — for example, the hydrogen atom — when in a condition which will be discussed in the chapter on the Electrolytic Dissociation Theory. But the value of this ratio for the hydrogen atom, as above, is perhaps a thousand times greater than its value for the corpuscle. Whence, the mass of the corpuscle is something like one-thousandth that of the hydrogen atom. Figures taken

from J. J. Thomson's "The Corpuscular Theory of Matter" follow: Value of the charge on a corpuscle, or on a charged hydrogen atom,  $10^{-20}$ , in electro-magnetic units; value of the ratio of charge to mass (in grams),  $1.7 \times 10^7$ .

Whence, the mass of the corpuscle is  $\frac{10^{-20}}{1.7 \times 10^7} g$ , or  $6 \times 10^{-28} g$ . The mass of the hydrogen atom may be placed at  $10^{-24} g$  (cf. p.12), which is thus some 1700 times the mass of the corpuscle.]

Wherever cathode particles impinge on the metallic anode or glass wall of the vacuum tube a series of etherial waves is produced. These are called Roentgen rays or X-rays. They are supposed to be single pulses traveling through the ether with the velocity of light, as distinguished from the continuous train of waves (thousands of waves succeeding one another in the same path in a fraction of a second) which produce the sensation of light. The thickness of these wave pulses is much less than the wave length of any kind of light, i.e., these waves might travel unimpeded in a much smaller tube than any of the light waves. They possess the power of penetrating many substances which are impervious to light waves, being absorbed by substances in proportion to their density. Thus, in passing through the body, more of the rays are absorbed by the bones than by the flesh, and if they then be allowed to fall upon a sensitized plate a strong contrast will develop. Aside from their action on the photographic plate, these rays cause certain substances to fluoresce or become luminous. A screen covered with such a substance (the fluoroscope) is commonly used in presenting an X-ray picture before the ordinary vision. The Roentgen rays are not deflected by an electrical or magnetic field. They "ionize" gases, or cause them to conduct the current by reason of the formation of corpuscles which carry the electricity.

In addition to the negative corpuscles discussed above, positive carriers of electricity are found in the vacuum tube. These travel towards the cathode and may be observed and studied in the region back of the cathode by using a cathode through which holes, or canals, have been bored. Hence, they are called canal rays. It has been found that the canal rays are deflected by an electrical or magnetic field in a manner to correspond with their positive charges; that they move much more slowly than the negative corpuscles; that the magnitude of the charge is never smaller than that on the negative corpuscle and that the ratio of mass to charge always possesses a value much smaller than the corresponding value in the case of the negative corpuscle — consistently indicating a particle of atomic dimensions.

Corpuscles are given out by all substances under some condition or other. Metals furnish them when raised to high temperatures. The negative corpuscles are invariably of the sub-atomic dimensions noted above. The positive particles are never inferior to the lightest known atom — the hydrogen atom — in point of mass. It is generally supposed that these positive particles are atoms, or groups of atoms, from which one or more negative corpuscles have been detached.

Of particular interest and importance is the spontaneous emission of charged particles from the atoms of radio-active substances. In this connection we will note primarily that three types of rays are emitted by these substances,

namely,  $\alpha$ ,  $\beta$  and  $\gamma$  rays; corresponding to the canal rays, cathode rays and Roentgen rays of the vacuum tube, respectively: and that the study of these phenomena has corroborated and amplified in large measure the conclusions derived from the preliminary study of the phenomena of the cathode tube. All three types of rays "ionize" gases — cause them to conduct — the  $\alpha$  rays being most efficient (by far) in this respect and the  $\gamma$  rays least efficient. It is owing to this property that the "activity" of a radio-active substance is easily susceptible to measurement. The substance is brought in the vicinity of a charged electroscope, when the air is rendered conductive and the charge is dissipated from the instrument. This test is extremely sensitive. A radium preparation must be some 150,000 times purer to respond to a test with the spectroscope (and radium is classed among the elements giving the most sensitive spectroscopic reaction) than is required for the electroscope test. (Descriptions of the spectroscope and its use may be read in Holleman-Cooper's "Text Book of Inorganic Chemistry," edition of 1908, p. 386, and Smith's "General Inorganic Chemistry," edition of 1907, p. 561.) On this account, accurate experimental results are obtained with the extremely slight quantities of radio-active substances which are alone available.

The calculated masses of the  $\alpha$  particles are such as to indicate that they may be atoms of a rare gas called helium. This substance has actually been obtained as a disintegration product of radium, whereby we note the first actual realization of a transmutation of the elements.

Several intermediate disintegration products of the radium atom have been recognized and named (emanation, radium-A, radium-B, etc.). It has been found that the expression,  $I_t = I_0 e^{-\lambda t}$ , shows the relation between the initial intensity ( $I_0$ ) of the radiations (measure of radio-activity) thrown off by one of these disintegrating bodies and the intensity ( $I_t$ ) at the end of a finite time. The letter  $e$  denotes the base of the natural logarithms, while  $\lambda$  is the disintegration constant for the particular radio-active substance under consideration. In other words,  $\lambda$  represents the fraction of substance transformed per unit time and is independent of the temperature and all other physical or chemical conditions. Obviously  $\lambda$  may be calculated from observations and the formula used to determine the length of time necessary for a given radioactive substance to disintegrate to any specified extent. Thus, a striking array of figures, giving the times required for successive radium products to become half transformed, has been prepared by Rutherford:

Ra-Em. → Ra-A → Ra-B → Ra-C → Ra-D → Ra-E → Ra-F → Ra-G  
 4 days 3 mins. 21 mins. 28 mins. 40 yrs. 6 days 143 days end product?

Further calculation leads Rutherford to the conclusion that the life of radium is about 2000 years.

So far as we know, these disintegration products do not correspond to any previous known chemical elements, nor have we definitely located the end product of the disintegration, in our list of elements. There are only three elements well enough known to appear in the generally accepted list, which are radio-active, namely, radium, thorium and uranium. The parent of radium is thought to be uranium — all known uranium ores contain amounts

of radium strictly in proportion to the amounts of uranium which they contain.

It is particularly to be emphasized that the amounts of energy which are concerned in these remarkable sub-atomic alterations are enormous in comparison with the corresponding amounts which are associated with ordinary physical and chemical changes. For example, the heat evolved spontaneously by a gram of radium in an hour would be sufficient to raise its own weight of ice from the melting point to the boiling point. The total heat energy given out by a gram of radium during its life would be, according to Rutherford, about half a million times that liberated during the combination of enough hydrogen and oxygen to form a gram of water.

The  $\beta$  particles from radio-active bodies move at speeds varying from one-fifth to nine-tenths the velocity of light — much faster than the corresponding particles developed in the cathode tube. Now, experimental work has shown that, at these high speeds, the ratio of charge to mass is not constant. For velocities from zero to one-tenth the velocity of light only is this quantity essentially constant; at half the velocity of light a perceptible increase has occurred; while at nine-tenths the velocity of light a nearly two-fold increase is noted. If, then, we consider the charge to be invariable — which is in all probability true — we have a case in which the mass of a moving particle changes with the velocity. It has been demonstrated mathematically that a moving electric charge concentrated on a sphere of sufficiently small radius possesses inertia by virtue of the electromagnetic field of force created in the surrounding ether, i.e., it possesses apparent (electrical) mass. Further, elaborate calculations have been made, showing that if the mass of the moving particle were to be regarded as wholly electrical, it would increase just as the experiments indicate, with the velocity. This (calculated) increase becomes enormous as the velocity of light is approached, and it is significant, in this connection, that the observed velocities never equal the velocity of light, at which this electrical mass would reach an infinite value. No smaller charges of electricity than those associated with (constituting?) the  $\beta$  particles have ever been indicated by theoretical or experimental efforts. It is possible that these units of energy, apparently ponderable, i.e., possessing the most distinguishing characteristic of matter, in their career of rapid motion, are themselves responsible for the material nature of the atom, which latter may be regarded as a self-contained system of these units in orbital motion around one another under mutual governing influences. A radio-active, or unstable atom, expels a corpuscle or collection of corpuscles and suffers readjustment. Although such definite conceptions are highly speculative and the reader may never learn what matter of energy really is, we may safely say that the question of correlation of the conceptions, matter and energy, no longer appears in a wholly visionary aspect.

Study of the gaseous state, in which the molecules must be farthest removed from one another (since matter in this form occupies the greatest space per unit mass) and least subject to

mutual influences, has proved most fruitful in developing our present conceptions of matter. Prior to 1808, when **Gay-Lussac** (Paris) published the results of experiments showing that *gaseous elements combine in simple proportions by volume and the volume of the resulting products, if gaseous, stands in some simple ratio to that of the reacting gases* (*law of Gay-Lussac*), the fundamental conception that an elementary substance is composed of two separate orders of particles was not prevalent among chemists. According to the original theory, most specifically advanced by **Dalton** (Manchester, Eng.), a few years earlier, indivisible "elementary atoms" were regarded as the ultimate particles of elementary substances, and "compound atoms" as the smallest integral parts of compound substances. It was clearly recognized that the numbers of elementary atoms concerned in any combination were never large.

The simple numerical relations of these "indivisible atoms" when united in the "compound atoms," taken in connection with the equally simple volume relations prevailing in the combination where gases alone were concerned, indicate equally simple relations between the numbers of so-called atoms, whether simple or compound, in equal volumes of the gases under consideration. **Boyle's Law:** *The volume of a gas varies inversely as the pressure if the temperature remains constant;* and **Charles' Law:** *The volume of a gas varies directly as the absolute temperature if the pressure remains constant,* unite in revealing striking conformity in the behavior of all gases, irrespective of their nature, when subjected to altered physical conditions. This points strongly to a conclusion that the volume, temperature, and pressure relations of gases are determined solely by the number of particles present in them. The simplest assumption would be that *equal volumes of all gases contain the same number of particles under the same conditions of temperature and pressure.* This fundamental conception, which has since been proven in complete harmony with the facts, was most definitely advanced by **Avogadro** (Turin) in 1811, who showed the necessity of modifying Dalton's original atomic theory by requiring that elementary matter, as well as compound matter, be regarded as divided into *two finite orders of particles*, of which the particles mentioned above — or the *molecules* previously noted — constitute the first order.

A clearer conception of the foregoing statement may be obtained by considering a typical example of gaseous combination. One volume of oxygen when combined with the requisite amount of hydrogen, furnishes two volumes of water vapor. Since, according to the hypothesis just presented, these two volumes of water vapor must contain twice as many particles (molecules) as the single volume of oxygen, and moreover, since each water particle must contain some oxygen, we are forced to conclude that a division of Dalton's supposedly indivisible oxygen particles has preceded combination.

The terms, **atom** and **molecule**, are in constant use among chemists. Whether we believe in the actual existence of either or both orders of particles is of little consequence. The fact of prime importance is, that *if matter were so constituted, it would appear as it now does*. Moreover, the introduction of such imaginative units aids us to intelligently study and systematize chemical phenomena. For practical purposes, it is necessary to associate with each particular kind of atom, a number which defines its most essential individual characteristic, that of **mass**. The absolute weight of any atom can only be estimated.\* On the other hand, we are quite able to deduce an accurate system of **relative weights** representing the smallest quantities of each element capable of participating in chemical reaction. These relative numbers are known as **atomic weights**, and are universally referred to the oxygen standard, which arbitrarily places the oxygen number at 16 times unity, or 16. More extended discussion of this subject follows in Chapter IV.

With these fundamental principles in mind, we are in a position to consider the complete argument by which experimental results relating to a given case of gaseous combination between the elements may be used to determine the composition of the resulting gaseous compound.

\* According to recent calculations by Lord Kelvin, the number of molecules ( $N$ ) in 1 cubic centimeter of a gas at  $0^{\circ}$  C., and 760 millimeters pressure, is  $10^{20}$ . 1 c.c. of hydrogen weighs about 0.00009 gram under these conditions. Hence, the weight of a hydrogen molecule is  $\frac{0.00009}{10^{20}}$ , or  $9 \times 10^{-25}$  gram, and that of a hydrogen atom ( $W$ ),  $4.5 \times 10^{-25}$  gram, since the hydrogen molecule contains two atoms, as will be shown shortly. According to Van der Waals' calculations, based on the kinetic theory of gases,  $N = 5.4 \times 10^{19}$  whence,  $W = 8.3 \times 10^{-25}$  gram.

One volume of hydrogen combines completely with one volume of chlorine to form two volumes of gaseous hydrochloric acid, if the three gases are measured under the same conditions of temperature and pressure. The accompanying diagram is of service in keeping these relations prominently in view during the discussion.

By experiment, one volume of chlorine is found to weigh about 35.5 times as much as one volume of hydrogen measured under the same conditions. Since the gases combine completely in this ratio, *to find the relative numbers of hydrogen and chlorine atoms in the resulting compound* it will be necessary to divide

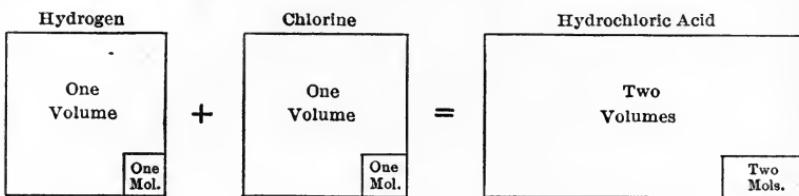


Fig. 1.

these ratio numbers by the corresponding relative weights of the atoms. It has already been noted that such relative weights may be readily determined. Without opening a discussion at this time (cf. Chapter IV), of the methods employed to yield these results, we may simply state that the atom of chlorine is known to be about 35.5 times as heavy as the atom of hydrogen. Dividing the ratio representing the combination of hydrogen and chlorine by weight,  $1 : 35.5$ , by the ratio representing the relative weights of hydrogen and chlorine atoms,  $1 : 35.5$ , we obtain a third ratio,  $1 : 1$ , which signifies that there are equal numbers of hydrogen and chlorine atoms in the compound, hydrochloric acid.

Suppose we start with  $x$  grams of hydrogen. The weight of one atom of hydrogen is 1 gram divided by the number of atoms

( $n$ ) making up this weight, or  $\frac{1}{n}$  g; and the number of atoms in  $x$  grams is,  $\frac{x}{\frac{1}{n}} = nx$ .

To combine with  $x$  grams of hydrogen,  $35.5x$  grams of chlorine are required. The weight of one atom of chlorine is 35.5 times

the weight of one atom of hydrogen, or  $\frac{35.5}{n}$  g; and the number of atoms in  $35.5x$  grams is,  $\frac{35.5x}{n} = nx$ , which is *identical with*  
*n*  
*the number of hydrogen atoms required for the combination.*

Purely chemical reasoning suffices to show that the *molecule of hydrochloric acid contains only one atom of hydrogen (and, consequently, one atom of chlorine)*; if more than one atom were present, it would be possible to obtain a class of derived compounds (acid salts) resulting from partial replacement of the original hydrogen in one molecule of acid by a metal. In the present case, no such derivatives are known. We are thus led to the complete conclusion that a molecule of hydrochloric acid consists of *one atom of hydrogen in combination with one atom of chlorine*.

Referring again to the volume relations between these three gases (p. 13), we note that, according to **Avogadro's Law**, the numbers of molecules in the gases are proportional to the volumes of the gases (see diagram, Fig. 1, p. 13, large and small areas). Therefore, when one *molecule* of hydrogen loses its identity, one *molecule* of chlorine participates in the change, and two *molecules* of hydrochloric acid are formed. Each molecule of acid contains one atom of hydrogen, as developed in the preceding discussion. Therefore, two atoms of hydrogen are contained in the total amount of acid which required one molecule of hydrogen in its formation. We are free to conclude that a *single molecule of hydrogen contains two atoms*.

Similar reasoning may be applied to show that the chlorine molecules are diatomic. All of the common gaseous elements, namely, hydrogen, oxygen, nitrogen, fluorine, chlorine, bromine, and iodine, are likewise composed of diatomic molecules, under the conditions which usually obtain.

We have already remarked briefly on the different forms of matter determined by the nature of aggregation of the constituent molecules. The **kinetic theory** carries us a step further in establishing an imaginative mechanical constructive view of matter, by introducing the additional energy factor. According to this

theory, the heat energy absorbed by substances during temperature elevation, or change of state, is mainly converted into molecular kinetic energy (energy due to motion of the molecules). Molecules constituting a solid are supposed to oscillate around a definite position of equilibrium, which is maintained by the very considerable attractive forces, supposed to operate between them in this close state of aggregation. The (perfectly elastic) molecules, when aggregated to form liquid matter, are capable of much more extended and energetic motion, causing mutual bombardment and a tendency to further separation. They are, nevertheless, closely enough associated to exert mutually attractive forces, sufficient in effect to overcome this disruptive tendency and to maintain a limited surface. The constituent molecules of a gas are least subject to mutual attraction and uniformly distribute themselves throughout any inclosing space, irrespective of its size.

It is easily apparent that such of the molecules within a liquid as reach the surface with a velocity greater than the average, will project themselves out into the space bounding the liquid (evaporate), and if this space is an enclosed one, will here attain a certain concentration (as vapor) determined by the average rate of mutual exchange across the bounding surface. The effect of heat addition to a liquid is to increase the molecular kinetic energy, causing more evaporation until eventually the liquid disappears.

The presence of a definite amount of vapor at a given temperature in the closed space above a liquid, determines a certain **vapor pressure** (pressure due to the molecular impacts against the inclosing walls) within this closed space. A vapor pressure magnitude, in this connection, is often referred directly to the liquid, when it represents the power of the latter to maintain vapor of this pressure, and is called the **vapor tension** of the liquid. As the temperature of a liquid is raised, its vapor tension increases. If the liquid is open to the air, it boils, or passes rapidly into vapor, when a temperature is attained at which its vapor tension is equal to the opposing atmospheric pressure.

Transformation of gaseous matter into liquid matter of the same kind is dependent on the temperature and pressure. If effected at some constant pressure, it is always abrupt,

accompanied by heat evolution, during which the temperature remains constant until complete transformation has occurred. By properly chosen successive variations of temperature and pressure, this change may result without discontinuity, i.e., we may effect a gradual and continuous change from gas to liquid, showing a close inherent relationship between the two states.

For each substance there always exists a **critical temperature**, above which it is impossible, no matter how great the compression, to liquefy the gas. This is reasonable, if we reflect that to liquefy a gas it is necessary that the kinetic energy of its molecules be adequately decreased and that they be brought closer together. Pressure accomplishes the latter object, but to completely attain the desired end, proper coincidence of the former condition must be secured by sufficient cooling.

Transformation from the liquid to the crystalline state is invariably discontinuous. It is, indeed, difficult to imagine any change from an isotropic to an anisotropic material other than abrupt. On the other hand, when an amorphous solid is produced by cooling a liquid, the change is gradual and continuous. There is no abrupt change of state. The change is rather one of degree, since the essential difference between an amorphous solid and a liquid lies in the lesser kinetic energy of the molecules when assembled to constitute the former (amorphous solid) material.

Finally, we recognize the capability of certain elementary substances to exist in more than one solid modification, possibilities including, besides the **amorphous** form, one or more specific crystalline varieties. This property is called **allotropism**. Such differences in form may be due to varying arrangements of the molecules in the solid material, or may be complicated by sub-grouping of these component particles — resulting in a final aggregation of clusters.

An elementary or compound substance, which occurs in two, three, or several different crystalline modifications, is called **dimorphous**, **trimorphous**, or, in general, **polymorphous**. Broadly speaking, these related solid modifications are, under specific conditions, interchangeable; energy change always associating itself with the transformation. Thus, the crystalline material, called  $\gamma$  iron, which is formed (heat evolution) on cooling pure molten iron when its freezing point, about  $1515^\circ$ , is reached,

undergoes two transformations before it becomes cold. At  $880^{\circ}$ , a second modification, called  $\beta$  iron, is formed spontaneously (heat evolution), and at  $780^{\circ}$ , a third modification, called  $\alpha$  iron, results. The temperatures at which such changes occur, are called *transition temperatures*. Reverse changes (heat absorption) would occur on heating  $\alpha$  iron. The last mentioned variety has no tendency to change its physical form at temperatures below  $780^{\circ}$  and is the common magnetic modification. At  $880^{\circ}$ , both  $\gamma$  and  $\beta$  iron may remain in contact without predisposition to alteration. If the temperature is raised above this point, all becomes  $\gamma$  iron; if lowered, all changes to  $\beta$  iron. Iron is, thus, trimorphous.

Again, a single atomic variety of matter, namely, the oxygen atom, exclusively constitutes the material part of two substances, totally different from one another in each of their three states of aggregation and in chemical properties. These substances are ordinary oxygen and ozone, both gases under ordinary conditions. Molecules of the former contain two atoms, while those of the latter contain three.

Closely similar conditions are presented by such compounds as possess the same percentage composition (contain the same kinds of matter in the same proportions by weight) in connection with different physical and chemical properties. We apply the term **isomeric** in describing this general condition and differentiate between two distinguishing cases: (a) those isomeric compounds which possess molecules of different mass, called **polymeric**; and (b) those isomeric compounds which possess molecules of the same mass and must, in consequence, owe their individuality solely to the configuration of atoms within the molecule. Such compounds are called **metameric**, or **physically isomeric**.

Evidently the gaseous state, in which the effect of attractive forces between the molecules, on account of their great distance from one another, reduces itself from a position of paramount importance to that of a merely modifying influence, presents conditions most favorable to extended development of the kinetic theory. In fact, the **Laws of Boyle, Charles, and Avogadro** may be deduced with extreme simplicity from this theory, neglecting the effect of such attractive forces. More-

over, satisfactory mathematical modifications have been made, on the basis of the theory, for the purpose of correcting inaccuracies to which these laws have been shown subject, when applied to highly concentrated, or compressed gases, in which the molecular attractive forces must attain real significance.

**Deduction of the Gas Laws from the Kinetic Theory.** (1) Boyle's Law: Consider a quantity of gas containing ( $n$ ) perfectly elastic molecules of individual mass ( $m$ ), inclosed in a cubical vessel an edge of which measures ( $l$ ) cm. Let the average velocity of these molecules be ( $v$ )  $\frac{\text{cm.}}{\text{sec.}}$ . If

one of the molecules strikes a bounding surface at right angles, assuming perfect elasticity of molecule and bounding wall, its direction of motion is reversed, the velocity remaining unchanged. Consequently, its momentum has changed from  $mv$  to  $-mv$ . This change in momentum,  $mv - (-mv)$ , or  $2mv$ , is a measure of the force, or pressure, exerted at the point of impact. In reality, the molecules preserve no regularity as to direction of motion, but we may resolve the velocity of each into three components,  $v_1$ ,  $v_2$ , and  $v_3$ , directed at right angles towards three sides of the cube. Then, we have the relation,  $v_1^2 + v_2^2 + v_3^2 = v^2$ . The molecule suffers a change in momentum of  $2mv_1$ , due to its component velocity,  $v_1$ , on striking one side of the cube. The number of impacts per unit of time as it travels back and forth between opposite sides, will be  $\frac{v_1}{l}$ ; its velocity divided by the number of centimeters traveled before each impact. The total change in momentum, due to motion in this direction is, then,  $\frac{2mv_1^2}{l}$ . Similarly, the changes in momentum, due to normal motion

between the two remaining pairs of surfaces, are  $\frac{2mv_2^2}{l}$ , and  $\frac{2mv_3^2}{l}$ . Addition of these three quantities gives, as total pressure effect for each molecule on all the walls,  $\frac{2m(v_1^2 + v_2^2 + v_3^2)}{l}$ , or,  $\frac{2mv^2}{l}$ . To obtain the pres-

sure corresponding to impacts of all the molecules on a unit area of surface, we must multiply the above expression by ( $n$ ), the number of molecules, and divide by  $6l^2$ , the total surface area. This operation gives the value,  $\frac{mnv^2}{3l^2}$ , which we may place equal to the gaseous pressure  $P$ .

Observing that  $l^2$  is the volume, which we may call  $V$ , this equation becomes,  $P = \frac{mnv^2}{3V}$ . Since none of the values,  $m$ ,  $n$ , and  $v$ , can vary if the temperature remains constant, the above equation shows that the

pressure of a gas varies inversely as the volume, at constant temperature. This is one method of stating Boyle's Law.

(2) Charles' Law: The kinetic theory embraces a primary assumption that the square of the average velocity, with which the molecules of a gas move, is proportional to the absolute temperature. A glance at the transposed equation,  $V = \frac{mnv^2}{3P}$  (from the final equation in the preceding paragraph) shows that, for a constant value of  $P$  ( $m$  and  $n$  can change only with the nature and amount of gas), the volume varies directly as the square of the velocity. Consequently, the volume at constant pressure varies directly as the absolute temperature, as enunciated by Charles on experimental grounds.

(3) Avogadro's Law: If we consider identical volumes of two different gases at the same pressure, the  $PV$  expressions obtained by transposing the final equation given in (1) must be equal. Expressing the masses, numbers, and velocities of the different molecules by  $m_1, n_1, v_1$ , and  $m_2, n_2, v_2$ , respectively, we have the following equality;  $\frac{1}{3}m_1n_1v_1^2 = \frac{1}{3}m_2n_2v_2^2$ . There can be no difference in the kinetic energies of molecules composing different gases at the same temperature. Hence, we may write,  $\frac{1}{2}m_1v_1^2 = \frac{1}{2}m_2v_2^2$ . Dividing the first equation by the second, we obtain,  $\frac{2}{3}n_1 = \frac{2}{3}n_2$ , or,  $n_1 = n_2$ , the relation required by Avogadro's Law.

Reasoning from the kinetic theory, we would expect gases, irrespective of their nature, to mix completely when brought into contact. The constituent molecules, owing to their great separation and rapid motion, unhampered by mutual attractive forces of appreciable magnitude, could scarcely fail to interpenetrate. Experiment verifies this conclusion and shows, in addition, that the relative rapidity of such intermixture, or diffusion, of gases is inversely proportional to the square roots of their densities, a result which may itself be significantly deduced from the theory.

For this purpose, consider the equation,  $P = \frac{mnv^2}{3V}$ , derived in the discussion relative to Boyle's Law. Solving for  $v$ , we obtain,  $v = \sqrt{\frac{3PV}{mn}}$ . But,  $\frac{mn}{V}$  is an expression for the density of a gas, i.e., the total mass of molecules divided by the volume. Substituting *density* for this expression in the above equation, we have the relation,  $v = \sqrt{\frac{3P}{\text{density}}}$ , which shows

that  $v$  is inversely proportional to the square root of the density. Now,  $v$  represents the average velocity of the molecules composing a gas and must determine the rate at which it diffuses. Whence, the rate of diffusion is inversely proportional to the square root of the density.

The assumption of appreciable attractive forces (cohesion) between the molecules of a substance when in the solid or liquid state, would suggest resistance to any interpenetration by molecules of another kind. On the other hand, the existence of attractive forces between different kinds of molecules (adhesion) would promote such interpenetration. Different liquids, or solids, would, then, intermix until these opposing forces attained equilibrium in the mixture. As a matter of fact, endless variety is observed in the degree of intermixture, or *miscibility*, between different solids and liquids. Complete miscibility, complete immiscibility, or any intermediate degree of miscibility may occur. The degree of miscibility will vary with the temperature, since the relative values of cohesive and adhesive forces depend on the temperature. Thus, molten zinc and molten lead mix completely somewhat above  $900^{\circ}$ , while, at  $700^{\circ}$ , 92 parts of zinc will mix with 8 parts of lead, and 81 parts of lead will mix with 19 parts of zinc, both liquids remaining sharply separated when in contact. Molten gold and silver mix completely and, on cooling, form a crystalline solid, likewise characterized by complete intermolecular mixture. The individual crystalline particles composing such a mixture are called *mixed crystals*.

When a solid is brought into contact with a liquid, its molecules may mingle to a greater or lesser degree with the molecules of the liquid. The solid is said to **dissolve** in the liquid, forming a **solution**. We use the term **solubility** to define the amount of a given solid which a unit amount of liquid, or **solvent**, will dissolve. Solubility varies with the temperature.

The **concentration** of a solution is the amount of dissolved substance contained in a unit volume of solution. A **saturated solution** contains the maximum amount of material which will dissolve at the given temperature.

Gases may dissolve in liquids. The extent of such solubility depends primarily on the nature of gas and liquid, but, in any specific case, is *directly proportional to the pressure of the gas*,

provided both pressure and solubility are relatively small. The latter generalization, known as **Henry's Law**, is clear in the light of our theory: Rapidly moving molecules from the gas penetrate the liquid surface, continuing in their motion within the liquid and accumulate here until their rate of reciprocal projection into the gas becomes equal to their rate of entry. The rate at which these molecules enter the liquid is proportional to the number of impacts per unit time, which is, in turn, proportional to the gaseous pressure. Hence, an increase in pressure must require a greater concentration of "gas molecules" in the liquid to determine a rate of expulsion equal to the increased rate of reception.

Excessive solubility of a gas in a liquid is due to chemical action. One volume of water dissolves more than 1000 volumes of ammonia at 0° C., 760 mm. pressure. In this case, a new substance, called *ammonium hydroxide*, is formed as the result of such action.

A liquid dissolves the individual constituents of a gaseous mixture independently (assuming no chemical action in the system). The solubility of each gas is determined exclusively by its own *partial pressure* (the pressure which it contributes towards the total pressure).

The student will readily recognize the practical necessity of uniformly adopting some convenient and concise written method of rendering the composition peculiar to each known chemical compound apparent at a glance. The conventional practice employed by all chemists to realize this necessity consists primarily in ascribing to each element a **symbol**, which abbreviates its (common or Latin) name to one large letter (or two letters, the first of which is large), and implies an associated atomic weight characteristic of the substance. A list of symbols with atomic weights will be found inside the cover of this book. To indicate the exact composition of a given compound, proper symbols are arranged side by side, with added subscripts, which denote the number of individual atomic weight units (if greater than 1) composing a single molecular weight unit. Such an arrangement of symbols is called a **formula**. Single molecules of the substances *sodium chloride* and *potassium chlorate*, for example, are represented by the formulas, NaCl and KClO<sub>3</sub>.

When it is necessary to indicate more than one molecule of a compound, a numerical coefficient is placed before the formula.

Before proceeding further, it is essential that the true significance of the terms, **atomic weight** and **molecular weight**, be perfectly clear to the student. As previously noted, we are unable to ascertain the exact weights of individual atoms, but very accurate ratios of the weights of these different atoms may be determined. These numbers, consistently referred to the oxygen standard, O = 16.00, are the practical units, called *atomic weights*, which are indispensable to all chemical calculations. Simple addition of the numbers produced by multiplying each individual atomic weight corresponding to the symbols in a formula, by the associated subscript number, gives the molecular weight of the substance. Thus we see that *molecular weights* are also relative numbers based on the oxygen standard. A formula, to give the actual molecular weight of a substance, must represent not only the relative atomic proportions of each element involved, but the exact number of different atomic quantities in a unit molecular quantity. Thus, the formula  $\text{KClO}_3$  correctly represents the composition and molecular weight of potassium chlorate, while the formula  $\text{K}_2\text{Cl}_2\text{O}_6$  represents only its composition with accuracy.

Atomic and molecular weights, as defined above, are quite as valuable for all stoichiometrical calculations, as the true weights of atoms and molecules would be. For example, if we know that the material composition of the substance *potassium chlorate* corresponds to the formula  $\text{KClO}_3$ , and that the relative weights of *potassium*, *chlorine*, and *oxygen* atoms are 39.1, 35.5, and 16 (all of which is implied by the symbolic notation), it is clear that 39.1 parts (by weight) of *potassium*, 35.5 parts of *chlorine*, and 48 ( $3 \times 16$ ) parts of *oxygen*, compose a total of 122.6 parts of *potassium chlorate*, and we are in a position to calculate the percentage composition of the compound at once.

By way of further illustration, if all the *potassium* in 122.6 weight units of *potassium chlorate*, namely, 39.1 units, be brought by direct or indirect chemical operation from its present state of combination into the entirely different chemical relationship expressed by the formula  $\text{KNO}_3$ , it is evident that  $39.1 + 14 + (3 \times 16)$ , or 101.1 units of this new compound *potassium nitrate*

will be formed. In other words, every time one *formula weight* of *potassium chlorate* is used, one *formula weight* of *potassium nitrate* is produced. Similarly, it would require all the potassium in two *formula weights* of *potassium chlorate*, or *potassium nitrate*, to produce one *formula weight* of *potassium sulphate*,  $K_2SO_4$ .

We may summarize the results of this reasoning by writing:



which reads, two molecules (or  $2 \times 122.6$  parts by weight) of potassium chlorate **are equivalent to** two molecules (or  $2 \times 101.1$  parts by weight) of potassium nitrate; **are equivalent to** one molecule (or 174.2 parts by weight) of *potassium sulphate*. It should be fully understood that the above **equivalents** are based on the *potassium* content of the compounds.

When sufficient data relating to a given compound are available, its formula may be calculated. Discussion of this subject follows in Chapter V. This constitutes the first step in establishing the nature of the compound. Examination of formulas in general reveals, at a glance, points of similarity in the constitution of the different substances along many and varied lines. This, of course, proceeds hand in hand with certain similarities in chemical behavior. In particular, we observe the tendency of well defined *groups* of atoms, which are incapable of existing alone in such state of combination, to maintain their individuality throughout chemical change; that is, to collectively combine with different substances.

Further comparison of formulas forces the conclusion that **each atom or group possesses a certain specific capacity for combination**, which determines the number of other atoms or groups with which it may unite. It cannot be stated that every elementary substance or group, as defined above, is capable of combining with every other elementary substance or group. In fact, most of the common inorganic compounds represent the union of certain elements or groups, which may constitute a **positive list**, with certain other elements or groups, which may be assembled in a **negative list**. In case of combination between positive and negative members, according to this classification, the capacity for combination, or **valence**, of each assumes a rather definite value; that is, it is seldom modified by the nature

\* The sign  $\equiv$  is used throughout this text in the sense of *is or are equivalent to*.

of the combination. For example, on comparison of the formulas  $H|Cl$ ,  $Na|Cl$ ,  $H|NO_3$ ,  $Na|NO_3$ ,  $H_2|SO_4$ , and  $Na_2|SO_4$  (positive part to the left of dotted line, negative part to the right), we readily observe that hydrogen and sodium possess the same capacity for holding chlorine in combination, also the same capacity for holding the  $(NO_3)$  group, and finally, the same capacity for holding the  $(SO_4)$  group. The above phraseology is not intended to suggest that either hydrogen or chlorine plays the aggressive part in determining combination;—we know little regarding the nature of forces binding the atoms in chemical combination.

It is customary to assign a numerical value to the valence of each atom or group, consistently referred to hydrogen as unity. Thus, Cl,  $(NO_3)$ , and Na, each have a valence of 1, and  $(SO_4)$ , a valence of 2. The formula of aluminium chloride is  $AlCl_3$ ; whence, the valence of aluminium is 3.

Some elementary substances form two well defined series of compounds, corresponding to two separate valence values. In this connection, we may mention *monovalent copper*, forming *cuprous* compounds, such as  $Cu_2Cl_2$  or  $Cu_2SO_4$  and *bivalent copper*, forming the corresponding *cupric* compounds  $CuCl_2$  and  $CuSO_4$ . Other examples will confront the student from time to time. It is essential to rapid progress in chemical study, that the principle of valence be used as an aid to the memory in acquiring familiarity with chemical formulas.

With regard to those compounds formed between two positive or two negative elements, it may be remarked, in general, that no such simple deduction of probable formula types is admissible. The specific nature of such combination appears to greatly modify the combining capacity of each constituent. By way of illustration, univalent sodium and bivalent cadmium form the compound  $NaCd_2$  but fail to unite in the more logical proportions  $Na_2Cd$ . In conclusion, it may be stated that this class of compounds is of comparative unimportance. The general value of the valence principle to the beginner is not seriously impaired by exceptions noted under this category.

The most comprehensive classification of inorganic chemical compounds, according to related chemical properties and analogous constitution, recognizes three quite distinct types, which are named **acids, bases, and salts**.

An **acid** always contains hydrogen in combination with some non-metal, or characteristic group of elements including oxygen. The term, *acid radical*, is often applied to such a group. Properties common to all acids are primarily determined by their essential constituent, *hydrogen*, in its characteristic relationship to the other atoms. In particular, we note that this *acid hydrogen* is invariably capable of being replaced by a metal. Hence, it is often called *replaceable hydrogen*.

A **base** consists of a metal (or group which may be regarded as equivalent to a metal) in combination with the (OH) group. This group may be replaced by an acid radical.

The chemical nature of **salts** is best understood by considering their relationship to acids and bases. Thus, to obtain the typical formula of a salt, we substitute a metal for hydrogen in the typical formula of an acid, or an acid radical for the (OH) group in the typical formula of a base.

An acid containing one atom of replaceable hydrogen in its molecule is called **monobasic**.\* If the number of replaceable hydrogen atoms is greater than one, the term **polybasic** (**dibasic**,\* **tribasic**, etc.) is applied. In addition to the **normal salts**, derived from an acid by replacing its (acid) hydrogen completely with a metal, a somewhat different type of derivative may be obtained from a polybasic acid by replacing part of its hydrogen by a metal. Such a compound is called an **acid salt**. Similarly, a base, the molecule of which includes more than one (OH) group, may furnish salt-like derivatives, which still contain this group. A compound of this nature is called a **basic salt**. It is, perhaps, more common for the composition of a basic salt to indicate combination between one or more molecules of the base and one or more molecules of the normal salt, and for that

\* Indicating that the hydrogen in one molecule of acid may be replaced by the metal in one molecule of the simplest kind of a base, i.e., that containing one (OH) group. Thus, HCl is a monobasic acid — from HCl and NaOH, we may obtain NaCl. As an example of a dibasic acid, we may cite  $H_2SO_4$ . In this case, two molecules of the base NaOH are required for the replacement —  $H_2SO_4$  with 2NaCl gives  $Na_2SO_4$ . If the base contains two (OH) groups, only one molecule is required for the latter replacement — Ca(OH)<sub>2</sub> and  $H_2SO_4$  give  $CaSO_4$ . The terms, monacid base and diacid base are sometimes used to characterize bases with respect to the number of their replaceable (OH) groups.

of an acid salt to indicate similar combination between the acid and normal salt.

Simplest among inorganic acids are the **binary acids**, which contain no oxygen, but consist of one other elementary substance in combination with hydrogen. The termination *-ic* is used in naming these acids, while the termination *-ide* is applied in designating their salts. This latter termination is also applied, without reservation, to the names of all other binary compounds, i.e., oxides, nitrides, phosphides, etc.

The same elementary substance (in combination with hydrogen and oxygen) often forms two or more **oxygen acids**. In such cases, the ending *-ic* is arbitrarily employed in naming one of them, while the ending *-ous* characterizes another containing relatively less oxygen. The endings *-ate* and *-ite* respectively, are used in naming salts derived from these acids. Finally, the prefix *hypo-* in combination with the ending *-ous* is employed in naming a possible acid in this series containing still less oxygen, and the prefix *per-* in connection with the ending *-ic* in naming a member containing more oxygen than the first. Corresponding salts are named *hypo-ite* and *per-ic*.

Two or more salts sometimes combine in definite proportions to form a type of compound, called a **double salt**, which is rather easily resolved into its constituent salts. Quite different in nature are the **mixed salts**, in which the constituents of two closely similar salts are found partially replacing one another in equivalent proportions.

A salt, or double salt, frequently combines with a definite molecular proportion of water on crystallization from aqueous solution. Such compounds are called **hydrated salts**. Their constituent water is readily removed by heating, in some cases, spontaneously on exposure to the air (efflorescence).

Oxides of the non-metals usually combine with water to form acids. Such oxides are called **acid anhydrides**. If the oxide fails to combine directly with water, it is, nevertheless, acidic in character, tending to react with bases, or basic oxides, to form salts.

Oxides of the metals are basic in character, often combining with water to form **metallic hydroxides**, or bases. The oxides of certain elements are less definite in their chemical nature.

exhibiting basic properties towards strong acids, or acidic oxides, and acidic properties towards strong bases, or basic oxides.

The following list of examples should be studied in connection with the definitions on the last two pages:

Acid.	Formula.	Base.	Formula.	Salt.	Formula.
Hydrochloric . . . . .	HCl	Calcium hydroxide	Ca(OH) <sub>2</sub>	Calcium chloride	CaCl <sub>2</sub>
Nitric . . . . .	HNO <sub>3</sub>	Ferric hydroxide	Fe(OH) <sub>3</sub>	Ferric nitrate	Fe(NO <sub>3</sub> ) <sub>3</sub>
Nitrous . . . . .	HNO <sub>2</sub>	Potassium hydroxide	KOH	Potassium nitrate	KNO <sub>3</sub>
Sulphuric . . . . .	H <sub>2</sub> SO <sub>4</sub>	Zinc hydroxide	Zn(OH) <sub>2</sub>	Zinc sulphate	ZnSO <sub>4</sub>
Sulphurous . . . . .	H <sub>2</sub> SO <sub>3</sub>	Barium hydroxide	Ba(OH) <sub>2</sub>	Barium sulphite	BaSO <sub>3</sub>
Hypochlorous . . . . .	HClO	Sodium hydroxide	NaOH	Sodium hypochlorite	NaClO
Chlorous (hypothetical) . . . . .	HClO <sub>2</sub>	Sodium hydroxide	NaOH	Sodium chlorite	NaClO <sub>2</sub>
Chloric . . . . .	HClO <sub>3</sub>	Sodium hydroxide	NaOH	Sodium chlorate	NaClO <sub>3</sub>
Perchloric . . . . .	HClO <sub>4</sub>	Sodium hydroxide	NaOH	Sodium perchlorate	NaClO <sub>4</sub>
Acetic . . . . .	H . C <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	Sodium hydroxide	NaOH	Sodium acetate	NaC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>

Acid Salt.	Formula.	Basic Salt.	Formula.
Sodium acid sulphate . . . . .	NaHSO <sub>4</sub>	Basic ferric acetate . . . . .	Fe(OH) <sub>2</sub> C <sub>2</sub> H <sub>3</sub> O <sub>2</sub>
Sodium acid carbonate . . . . .	NaHCO <sub>3</sub>	Basic lead carbonate . . . . .	2PbCO <sub>3</sub> .Pb(OH) <sub>2</sub>
Calcium acid carbonate . . . . .	CaCO <sub>3</sub> . H <sub>2</sub> CO <sub>3</sub>	Basic bismuth nitrate . . . . .	Bi(OH) <sub>2</sub> NO <sub>3</sub>

Mixed Salt.	Formula.
Sodium-potassium carbonate . . . . .	NaKCO <sub>3</sub> (The (2) negative valences of CO <sub>3</sub> are neutralized by the added (1+1) positive valences of Na and K.)
Calcium chloride-hypochlorite . . . . .	Ca(Cl)OCl (Ca <sup>Cl</sup> OCl)
Hydrated Salt.	Formula.
Copper nitrate . . . . .	Cu(NO <sub>3</sub> ) <sub>2</sub> . 3H <sub>2</sub> O
Zinc sulphate . . . . .	ZnSO <sub>4</sub> . 7H <sub>2</sub> O
Hydrated Double Salt.	
Ferrous ammonium sulphate . . . . .	FeSO <sub>4</sub> . (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> . 6H <sub>2</sub> O
Alum . . . . .	K <sub>2</sub> SO <sub>4</sub> . Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> . 24H <sub>2</sub> O
Acid Anhydride.	Corresponding Acid.
Sulphur dioxide, SO <sub>2</sub> . . . . .	Sulphurous acid, H <sub>2</sub> SO <sub>3</sub>
Sulphur trioxide, SO <sub>3</sub> . . . . .	Sulphuric acid, H <sub>2</sub> SO <sub>4</sub>
Phosphorus pentoxide, P <sub>2</sub> O <sub>5</sub> . . . . .	Phosphoric acid, H <sub>3</sub> PO <sub>4</sub> , and others

Silica, SiO<sub>2</sub>, is a common example of an acidic oxide which fails to form an acid on treatment with water.

Basic Oxide.	Formula.
Silver oxide.....	$\text{Ag}_2\text{O}$
Calcium oxide (lime) .....	$\text{CaO}$
Ferric oxide.....	$\text{Fe}_2\text{O}_3$
Cupric oxide.....	$\text{CuO}$
Cuprous oxide.....	$\text{Cu}_2\text{O}$
Magnesium oxide (magnesia) .....	$\text{MgO}$
Aluminium oxide (alumina). .	$\text{Al}_2\text{O}_3$

It is a common practice among chemists to express symbol weights, or atomic weights, and formula weights, or molecular weights, directly in grams, thus introducing the descriptive terms: **gram atom**, and **gram molecule**. Amounts of different substances which stand in direct proportion to their atomic, or molecular weights, are called **atomic** and **molecular quantities**, respectively. For example, in round numbers, 64 grams of copper, 108 grams of silver and 207 grams of lead constitute one gram atom\* of each metal, respectively. One gram molecule of sulphuric acid is about 98 grams, of nitric acid — 63 grams. The above amounts are atomic and molecular quantities respectively.

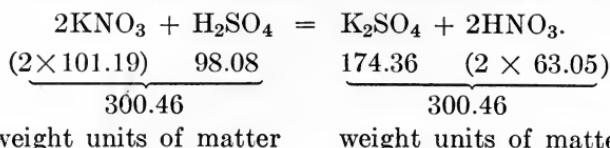
The result of any chemical reaction is a more or less complete change from one set, or system, of material, to another set, or system, without loss of matter. If the formulas of all substances concerned in the change are known, a **chemical equation**, representing the change in detail, may be constructed according to the following général outline: Form an expression indicating the summation of different molecules composing the original system, and an analogous expression embracing the different molecules present in the resulting system. Equate these two expressions, by assigning such numerical coefficients to each (molecular) formula as will render the sum of all the atoms of each variety equal on both sides of the equation. For example, let it be known that *potassium nitrate* and *sulphuric acid* react under conditions which result in the exclusive and complete formation of *potassium sulphate* and *nitric acid*. The systems present before and after chemical reaction are (1)  $\text{KNO}_3 + \text{H}_2\text{SO}_4$  and (2)  $\text{K}_2\text{SO}_4 + \text{HNO}_3$ .

It is at once apparent that two molecular quantities of *potassium nitrate* must be taken to furnish sufficient *potassium* for one

\* Cf. Table of Atomic Weights inside cover.

molecular quantity of *potassium sulphate*, and that one molecular quantity of *sulphuric acid* is required to deliver the complementary amounts of *sulphur* and *oxygen* necessary to complete this formula. At the same time, two atomic quantities of *nitrogen*, six of *oxygen*, and two of *hydrogen*, await further disposition. These are, however, the exact amounts needed to form two molecular quantities of *nitric acid*.

The properly balanced equation, therefore, reads:



Numbers, representing molecular quantities of the matter involved, are added in order to more clearly demonstrate the quantitative relations. They are, of course, omitted in the general formulation of chemical equations, being implied by the symbols, etc.

By far the greater number of chemical operations, which form the experimental basis of an introductory course in general chemistry, effect complete transformation of one set of substances, when taken in equivalent proportions indicated by the corresponding equation, into another set of substances, also specifically defined by the equation. Thus, *potassium nitrate* and *sulphuric acid*, when taken in the proportions 202.38 : 98.08, and heated moderately for a sufficient length of time, will evolve 126.1 units of gaseous *nitric acid*, and leave a residue of 174.36 units of *potassium sulphate*.

If the operation is conducted in a closed receptacle of relatively small volume, **transformation will not be complete**. A certain proportion of *potassium nitrate* and *sulphuric acid* will have been transformed into *potassium sulphate* and *nitric acid*, moreover, in such a way that for every formula weight of *potassium sulphate* in the mixture, there will be two formula weights of *nitric acid*, and for every formula weight of *sulphuric acid* remaining there will be two formula weights of *potassium nitrate*. In other words, the substances will have reacted according to the above equation, but the final result is a mixture of all four, perfectly indifferent in the presence of one

another, i.e., in **equilibrium**. If all the material at the start had been in the shape of *potassium sulphate* and *nitric acid*, the same identical mixture of four substances would have resulted, under similar working conditions. That is, the reaction may progress in both directions.

The sign of equality, implying complete transformation towards the right, does not properly apply to a reaction when carried out under conditions which render it incomplete in either direction (i.e., reversible). Two reversed arrows ( $\rightleftharpoons$ ) are used in such cases.

No feature of chemical study causes the beginner more trouble than **equation writing**. The erroneous impression often prevails that, once given the left-hand member of an equation, some mechanical-mathematical process of rearranging symbols will suffice to produce the complementary right-hand member. It must be emphasized that the identity of substances formed by chemical action is directly ascertained by experiment, or logically predicted by deference to well recognized chemical principles. The final balancing process alone is independent of such chemical reasoning and observation. Any student who acquires familiarity with the more general types of chemical action and is capable of writing formulas with facility, will find little difficulty in correctly formulating equations.

Some of these **general types of chemical reaction** may be briefly outlined at this juncture:

A single substance is often resolved into simpler substances by heat or other agency. Such change is known as **decomposition**. Zinc carbonate is decomposed into zinc oxide and carbon dioxide when strongly heated:  $ZnCO_3 = ZnO + CO_2$ .

An equally simple chemical change consists in the direct **combination** of two or more substances when properly handled. Copper and sulphur combine at a temperature approximating low redness:  $Cu + S = CuS$ .

Two salts may react in such a way that the total change would correspond to a primary decomposition of each, followed by an altered recombination of the parts. Change of this sort, called **double decomposition**, occurs when ammonium sulphate and sodium chloride are moderately heated:



Double decomposition in solution is frequently indicated by the **precipitation**, or deposition, of a reaction product (insoluble). The remaining product may usually be obtained in the solid form by subsequent evaporation of the solution. If no precipitation occurs, the less soluble substance will separate first (as a solid) on evaporation. The nature of such changes is discussed at some length in Chapters VII and VIII.

Reaction between a compound and an elementary substance frequently results in the **replacement**, and consequent liberation of some part of this compound by the added material. Metals commonly replace the hydrogen of acids:  $Zn + H_2SO_4 = ZnSO_4 + H_2$ . A halogen displaces any other halogen of greater atomic weight, from its binary compounds:  $Cl_2 + 2KBr = Br_2 + 2KCl$ .

**Acid and basic substances interact to form salts:**  $CaO + SiO_2 = CaSiO_3$  (at high temperatures),  $NaOH + HCl = NaCl + H_2O$  (base and acid—**neutralization**),  $ZnO + 2HCl = ZnCl_2 + H_2O$  (metallic oxide and acid).

Concentrated sulphuric acid reacts on the salt of a volatile acid, according to the following typical equation:  $H_2SO_4 + 2NaCl = Na_2SO_4 + 2HCl$ . The volatile acid (HCl) escapes from the mixture and a sulphate remains.

The chemical behavior of oxides towards water has been noted on page 26.

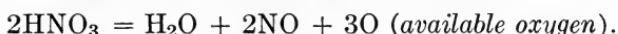
Particular attention must be directed to the **bearing of oxygen on chemical change**. Many reactions embody chemical rearrangement of the constituent material, primarily caused by reapportionment of oxygen within the system. Among the great number of oxygen compounds, we readily distinguish between certain ones, which strongly resist any effort to remove their oxygen, wholly or in part, and others which suffer loss of oxygen with greater or less facility. Thus, water ( $H_2O$ ), carbon dioxide ( $CO_2$ ), silica ( $SiO_2$ ), alumina ( $Al_2O_3$ ), magnesia ( $MgO$ ), etc., represent extremely stable combination of oxygen with other elements, and may be expected to occur liberally as final products (perhaps further combined, according to their individual nature) of diverse chemical action. On the other hand, potassium chlorate ( $KClO_3$ ), mercuric oxide ( $HgO$ ), silver oxide ( $Ag_2O$ ), cupric oxide ( $CuO$ ), cuprous oxide ( $Cu_2O$ ),

etc., lose oxygen with the greatest ease, and are unlikely to remain intact when subjected to a variety of chemical treatment.

The process by which oxygen leaves one compound to combine with other substances, is termed **oxidation**, with respect to the material receiving oxygen, and **reduction**, with respect to the material losing it. A compound generally capable of effecting the oxidation of other substances is called an **oxidizing agent**. One which removes oxygen from some moderately stable state of combination is called a **reducing agent**.

The reaction  $\text{Fe}_2\text{O}_3 + 2\text{Al} = \text{Al}_2\text{O}_3 + 2\text{Fe}$  represents oxidation of aluminium by ferric oxide, as well as reduction of ferric oxide by aluminium.

Certain highly oxidized substances may lose part of their oxygen when treated with a compound susceptible to oxidation, leaving one or more decomposition products which are more stable with respect to their oxygen content. Thus, two molecular quantities of *nitric acid*, an active oxidizing agent, include three atomic quantities of *oxygen*, which are **available** for the oxidation of other material, while the remainder of its *oxygen* is almost invariably appropriated by its own *hydrogen* and *nitrogen*. The following hypothetical reaction illustrates this statement:

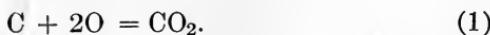


If charcoal, essentially *carbon*, is heated with concentrated nitric acid, *water*, *nitric oxide*, and *carbon dioxide* are recognized as final products of the ensuing reaction. An equation descriptive of this change may be constructed by using the proper formulas and introducing the numerical coefficients necessary to secure balance between both members:



Only the above set of coefficients (or equal multiples of them) will effect equality between both sides of the equation, and these numbers are best ascertained by the following deductive method, which, at the same time, effectively summarizes the chemical principles involved.

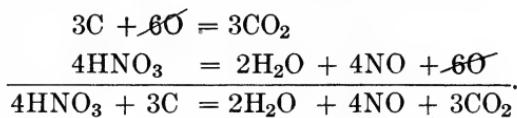
One atomic quantity of *carbon* requires two atomic quantities of *oxygen* for complete oxidation:



Some of the *oxygen* in *nitric acid* is *available* for this purpose, as we have previously noted:

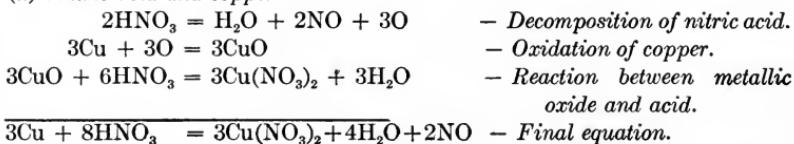


Since *nitric acid*, in a reaction of this kind, allows none of its *oxygen* to escape unused, equality between the amount furnished and the amount used must be established. This is effected by oxidizing three atomic quantities of *carbon* with the six atomic quantities of *oxygen* available from four molecular quantities of *nitric acid*. Thus, each coefficient in equation (1) must be multiplied by three, and each coefficient in equation (2) by two. On addition of both equations, *oxygen* (which is not a final product) is eliminated by cancellation from both sides, and there results a final (complete) equation, expressing the exact relations between reacting substances and final products:

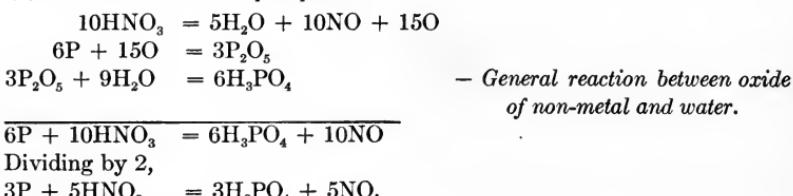


Additional examples will serve to emphasize the practical application of these principles:

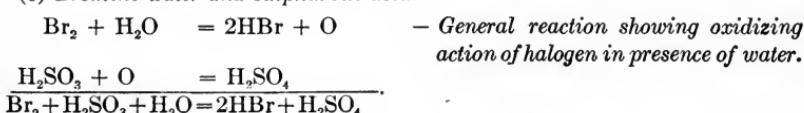
(a) *Nitric acid and copper.*



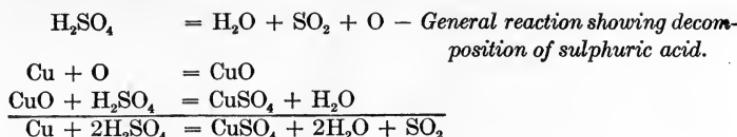
(b) *Nitric acid and red phosphorus.*



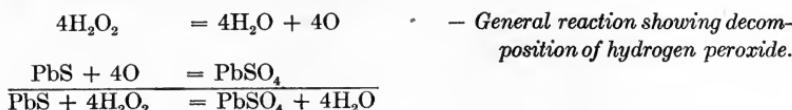
(c) *Bromine water and sulphurous acid.*



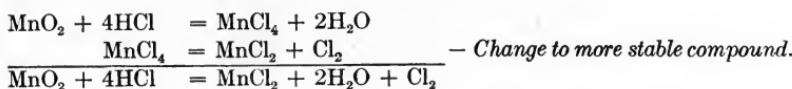
(d) Concentrated sulphuric acid and copper.



(e) Hydrogen peroxide and lead sulphide.

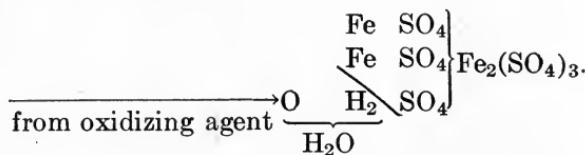


(f) Manganese dioxide and hydrochloric acid.

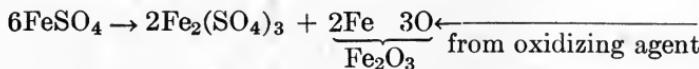


When more than one valence is associated with an element, properly chosen oxidizing agents change the compounds which correspond to its lower valence into those which correspond to its higher valence. Reducing agents accomplish the reverse change. These different valence conditions are often called different (higher and lower) states of oxidation.

Thus, to represent a transformation of *ferrous sulphate* ( $\text{FeSO}_4$ ) into *ferric sulphate* ( $\text{Fe}_2(\text{SO}_4)_3$ ) we require an additional *sulphate group* for every two molecules of the former compound taken. This may be obtained by oxidizing the *hydrogen* in one molecule of *sulphuric acid*:

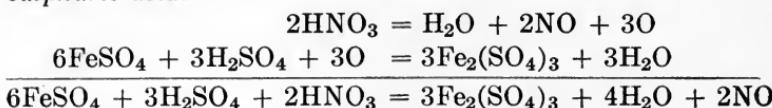


Or, if no free acid were present, part of the *iron* could be regarded as momentarily relieved from combination, and immediately thereafter subjected to complete oxidation:

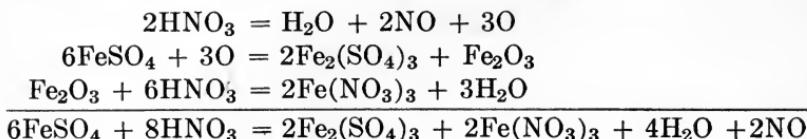


The complete changes follow:

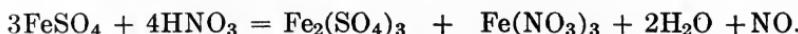
(1) *Oxidation of ferrous sulphate by nitric acid in presence of sulphuric acid.*



(2) *Oxidation of pure ferrous sulphate by nitric acid.*



Dividing by 2,

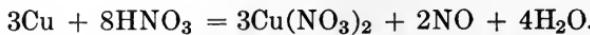


Complete oxidation of the *iron* to the *ferric state* is effected in (2), part of it forming *ferric sulphate*, and part, *ferric nitrate*.

The successive steps in the above work represent progressive *hypothetical* chemical change, which leads consistently to a correct final equation. We do not recognize in (2) for example, *oxygen* and *ferric oxide* as tangible intermediate products.

Since a chemical equation defines the relative quantities of all substances involved in a reaction, it is possible, if a definite amount of any one substance is given, to calculate the corresponding amounts of any or all the other substances. (Cf. p. 22.)

Problem: Calculate the amount of *cupric nitrate* formed when ten grams of copper react with an excess of nitric acid, using the equation:

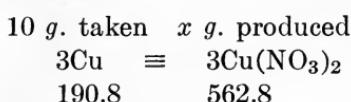


According to this equation, 190.8 weights of *copper* ( $3 \times$  atomic weight) require 504 weights of *nitric acid* ( $8 \times$  molecular weight) for reaction, thereby forming 562.8 weights of *cupric nitrate*, 60 weights of *nitric oxide*, and 72 weights of *water*. If an excess of *nitric acid* (i.e. more than is needed to react with all the copper) is present, just as much of it will be decomposed as is required by the *copper*. The total amount of *nitric acid*, in this case (assuming that the above equation applies without reservation as to

concentration, etc.), will have no bearing on the amount of *cupric nitrate*, etc., produced. Consequently, in calculating the amount of *cupric nitrate* produced from a given amount of *copper*, no attention need be paid to the *nitric acid*, nor to the *nitric oxide* and *water*, which are merely inevitable accessory products.

To solve a problem of this sort, select the essential formulas from the equation, indicate the proper equivalence between them and between the weights which they represent. Then make a simple proportion between these equivalent weights and the actual weights of the same substances, one of which is unknown ( $x$ ).

Thus, in the above case:



In substance, if 190.8 parts by weight of *copper* correspond to 562.8 parts of *cupric nitrate*, 10 grams of *copper* correspond to how many grams of *cupric nitrate*?

The correct proportion is:

$$190.8 : 562.8 :: 10 : x.$$

Solving,  $x = 29.5$  grams.

It seems hardly necessary to discuss possible variations in the form of such problems.

Students frequently fall into the error of using numbers which refer to volumes, and not weights (or to both indiscriminately) directly in these calculations. It is clear that all four terms of the simple proportion must represent weights, since two of them (molecular or atomic *weights*) do, by primary assumption. If a final result is required in volume units, instead of weight units, the latter must first be calculated, then properly transformed, by using a known relation between weight and volume for the substance in question.

Suppose we desire to know *how much hydrochloric acid must be used to neutralize five grams of sodium hydroxide*. The amount is readily calculated from the relation:



which follows from the equation:



Thus,  $40.06 : 36.45 :: 5 : x$ . Whence,  $x = 4.55$  g.

But, this is *pure hydrochloric acid*, a gas under ordinary conditions. We seldom handle the pure substance, using by preference, solutions containing definite amounts of the gas in water. Such a solution, containing 39.1 per cent of the pure acid by weight, has a density of 1.20 and is commonly known as *concentrated hydrochloric acid* (solution). A solution, of density 1.12, containing 23.8 per cent acid, is called *dilute hydrochloric acid* (solution).

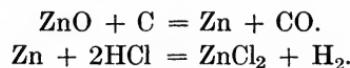
We would, in all probability, use the dilute acid for neutralization purposes, measuring, rather than weighing it. The weight of pure acid required in this case is known (4.55 g.). Consequently, it is necessary to know, in addition, the weight of *pure hydrochloric acid* in a unit volume of the solution. One cubic centimeter of this solution weighs 1.12 g. (Density = 1.12 compared to water — 1 c.c. water weighs close to 1 g. under laboratory conditions.) But, 23.8 per cent of this weight — 0.27 g. — is pure hydrochloric acid; the rest is water. That is, 1 c.c. of the solution contains 0.27 g. pure acid. To obtain 4.55 g. acid,  $\frac{4.55}{0.27} = 16.8$  c.c. dilute hydrochloric acid solution must be taken.

The volume of concentrated acid necessary for the same purpose is given by the operation,  $\frac{4.55}{(1.2)(39.1)}$ .

Frequently, we obtain a desired product as the result of several successive reactions, which represent necessary steps in the transformation of our original material. In such cases, we reckon the equivalence between original material and final product by noting each intermediate equivalence and use this as a basis for the single calculation needed to give the weight of final product resulting from a given weight of original substance.

Thus: *How many liters of hydrogen, measured at 0° C., 760 mm. pressure, may be produced by using 100 g. zinc oxide, according to the*

*following reactions? One liter of hydrogen weighs approximately 0.09 g. under these conditions.*



100 g.                    x g.

The properly ordered data reads:  $\text{ZnO} \equiv \text{Zn} \equiv \text{H}_2$ , and the  
81.4                        2.0

proportion : 81.4 : 2 :: 100 : x. Whence  $x = 2.46$  (grams hydrogen), and,  $\frac{2.46}{0.09} = 27.33$  (liters hydrogen).

## CHAPTER II.

### NATURAL CLASSIFICATION OF THE ELEMENTS.

It becomes apparent early in the course of chemical study that certain of the elements are closely related to one another in their chemical and physical properties. Further experience leads to a division of all the elements into several groups, each embracing a definite quota, the properties of which are broadly similar, but vary more or less gradually from one extreme to another through the several members.

The first of these natural groups usually presented to the beginner consists of four elements called the **halogens**; namely, fluorine, chlorine, bromine, and iodine. These elements are characterized by extreme reactivity towards other elements; in consequence, they are not found naturally in the free or uncombined state. All form binary hydrogen compounds, or halogen acids, of the same formula type: H — *Halogen*, stamping them as univalent towards hydrogen. The halogens do not show an equal tendency to combine with a given element, nor are the resulting compounds equally susceptible to decomposition, or possessed of the same properties. If such were the case, it would be difficult to recognize them as individual elements. But a marked gradation in any specific property, from fluorine through chlorine, bromine, to iodine, is always apparent. Thus, hydrofluoric acid HF is extremely stable; hydrochloric acid HCl is very stable; hydrobromic acid HBr is only moderately stable, its hydrogen rather available for reducing purposes; while hydriodic acid HI is very unstable — a valuable reducing agent.

This gradated behavior is very apparent on considering the oxidation phenomena produced by aqueous solutions of the halogens. When substances capable of oxidation are treated with chlorine water, they obtain oxygen as a result of the following decomposition:  $\text{Cl}_2 + \text{H}_2\text{O} = 2\text{HCl} + \text{O}\rightarrow$ . Chlorine water may

be kept fairly well without change unless brought into contact with a substance susceptible to oxidation. Fluorine decomposes water instantly. Bromine water and iodine water, in order, are less energetic oxidizing agents than chlorine water.

A more active halogen displaces a less active one from its binary compounds:  $\text{Cl}_2 + 2\text{KBr} = \text{Br}_2 + 2\text{KCl}$ ;  $\text{Br}_2 + 2\text{NaI} = \text{I}_2 + 2\text{NaBr}$ . The order of decreasing "activity" is Fl, Cl, Br, I.

Fluorine fails to combine with oxygen. The remaining halogens form oxides and oxygen acids, the salts of which are used as oxidizing agents on account of their instability. Towards oxygen, somewhat variable valence, never more than seven, must be ascribed to the members of this group.

The molecules of fluorine and chlorine are diatomic, even at very high temperatures. Those of bromine and iodine are diatomic at temperatures near the boiling points of these substances, but dissociate into monatomic molecules, iodine first, as the temperature increases.

The variation of physical properties in this group of elements consistently follows the order of chemical gradation. Thus, fluorine is a gas at ordinary temperature and under ordinary pressure, chlorine is a gas more easily liquefied than fluorine, bromine is a low boiling liquid, and iodine is a solid. The melting points, boiling points and other physical properties vary in steps from fluorine to iodine in the above mentioned order.

Without further extending this argument, we are in a position to clearly recognize a progressive relationship between these elements, when arranged in the order: Fl, 19.0; Cl, 36.45; Br, 79.96; I, 126.97. This is the order corresponding to the **numerical sequence of atomic weights** as shown by the associated numbers.

It remains to more closely examine the relationship between properties and atomic weights. An assumption that the properties of the different elements vary continuously with their atomic weights cannot be entertained, since, between two successive analogues,\* there exist a number of dissimilar elements having intermediate atomic weights. It is thus evident that, in a list of the elements arranged in the order of their atomic weights, a halogen will appear at intervals.

\* Substances possessing closely related properties.

At this point it is necessary, for the purpose of rendering the discussion more comprehensive, to anticipate some of the facts which will appear before the student, in greater detail, at a later time. Thus, the eight elements which possess smaller atomic weights than fluorine are: hydrogen, 1.008; helium, 4.0; lithium, 7.03; beryllium, 9.1; boron, 11.0; carbon, 12.00; nitrogen, 14.01; and oxygen, 16.00. All of these, except hydrogen, possess close analogues, which develop at intervals in the complete list of elements arranged according to increasing atomic weight, as we have pointed out relative to fluorine and its analogues.

It is of particular interest to ascertain how many dissimilar elements follow a given element before its analogue appears. We have remarked that the series of eight elements from helium to fluorine inclusive, are unlike. We now proceed to note that the ninth element, neon, 20, resembles helium; the tenth element, sodium, 23.05, resembles lithium and so on regularly until the sixteenth element, chlorine, 35.45, the analogue of fluorine, is reached. Thus, we observe a complete *series* or *period* containing eight dissimilar elements which bear an orderly resemblance to the eight dissimilar elements of a second period.

Continued application of this simple scheme does not result in an equally satisfactory arrangement of all the elements. For example, the eighth element following chlorine, manganese, 54.6, is not a halogen, although it bears some chemical analogy to the halogens. The next three elements, iron, nickel, and cobalt, find no analogues among the elements yet mentioned. Eighteen elements intervene between chlorine and the next halogen, bromine.

An adequate exposition of the periodic relations of all the elements (*Periodic System*) was first offered by **Mendelejeff** (St. Petersburg) in 1869. The following table closely imitates his classification:

TABLE OF THE ELEMENTS.

## THE PERIODIC SYSTEM.

In the table, vertical columns include *groups* of analogous elements. *Periods* are arranged horizontally. The groups are numbered 0-8. A general characteristic of each group is the most consistent valence of its members (1) towards hydrogen, or a halogen, and (2) towards oxygen. These valences are given under the group numbers, the symbol R standing for an element of the group in question, O for oxygen and X for hydrogen, or a halogen.

The first two periods have been discussed above. Reference has been made to additional complexity following these short periods. To secure logical arrangement, elements from argon, 39.9, to bromine, 79.96, are included in a long period, which is resolved into two short periods (1) argon-manganese, (2) copper-bromine, and three additional elements, iron, nickel, and cobalt. The members of these two short periods are consistently ordered in groups, 0-7, while the three extra elements constitute the primary members of Group 8. The remaining periods, except the last, are long.

It is to be observed that sub-grouping is followed after the advent of long periods. Elements composing the first sub-division of the long periods are collectively placed to the left in their corresponding groups; those composing the last sub-division are moved to the right. The members of such a sub-group (elements in vertical alignment), or natural group in the narrower sense, are very closely similar. In some cases, members of the left-hand sub-group are closely related to the two elements which head the group; in other cases members of the right-hand sub-group possess this relationship. Less often the connection is difficult to determine. In this table, the elements which are usually studied in an elementary course, are printed in bold figures.

Points of interest arise in considering the transition from one group to another in the table. Thus, no valence is associated with the noble gases (Group 0), as they show no tendency whatever to combine with other elements. The valence towards oxygen increases from one to eight as we pass from Group 1 to Group 8, while the valence towards hydrogen, or a halogen, increases from one to a maximum of four in Group 4, and then decreases regularly to one in Group 7. The most basic elements

which we have, the alkali metals, lithium, sodium, potassium, rubidium and caesium, stand next to the most indifferent, helium, neon, argon, krypton and xenon, while the whole table might be rolled vertically around a cylinder in such a manner that the strongly acidic halogens would bound these indifferent noble gases on the other side. All the non-metals (excepting those in Group 0), namely, boron, carbon, silicon, nitrogen, phosphorus, arsenic, oxygen, sulphur, selenium, tellurium, fluorine, chlorine, bromine, and iodine, are rather compactly placed in a triangular area of the table. Groups 3, 4, 5, 6, and 7 each begin with an acid-forming element and end with a base-forming element. As we pass from lower to higher atomic weight in these groups, acid properties become less prominent and basic properties develop.

The position of hydrogen in the table is uncertain. According to physical properties, as well as numerical relations, it should head Group 7. On the other hand, it shows analogy to the metals of Group 1, by combining in a similar way with negative elements or radicals.

Examination of the table reveals three inconsistencies in the arrangement according to increasing atomic weight: (1) The positions which argon and potassium should naturally assume, must be reversed to place them with their fellows. (2) Cobalt is placed before nickel, although possessing a greater atomic weight. Chemical analogies are more satisfactorily represented by this alteration, which associates cobalt with ruthenium and iridium; nickel with palladium and platinum. (3) Tellurium and iodine are transposed for a similar reason. There can be no question of the analogy between iodine and the preceding halogens, nor of that between tellurium and selenium. Careful revision of atomic weight determinations suggested by these abnormalities has failed to reveal error in the original consecutive numerical arrangement. Other apparent exceptions to the general scheme have been relieved from time to time, in this way. The value of the periodic system in criticising atomic weight values is further noted in Chapter IV.

Although the numerical difference in atomic weight between two successive elements is not uniformly the same, it is always small and not widely divergent. The mean difference for the first ten elements is 2.34, for the ten elements from silver to cerium (well along in the table) it is 3.23, somewhat larger. We note that, in certain cases, two successive elements in a list con-

taining all the known elements arranged in the order of increasing atomic weight, show a numerical difference between their atomic weights, which is much greater than the above mean difference. This points to the probable existence of undiscovered elements, best evinced by the necessity of leaving blank spaces in the table to secure proper arrangement according to analogies. By way of specific illustration, we may observe the positions of nickel and copper in the table. Copper shows no analogy to the He-Xe family, and is advanced to a more fitting place in Group 1. An unknown rare gas of atomic weight approximating 61, may, however, exist. Again, no known elements are closely related to manganese. Suggestive openings occur between molybdenum and ruthenium (atomic weight difference 5.7) and between tungsten and osmium (atomic weight difference 7), possibly corresponding to unknown elements which, together with manganese, might constitute a well-defined sub-group.

A number of elements have been discovered since the first presentation of the periodic table by Mendeleeff. It is a particularly impressive fact that his elaborate predictions concerning the probable nature of several of these elements, based upon a series of interpolations between the properties of adjacent elements, have been since realized with remarkable conformity.

We have not attempted, in the foregoing discussion, to closely follow the specific nature of analogies, chemical and physical, in each group. It is hoped that the student who has studied chemistry only a few months will find these introductory remarks of value in obtaining some adequate conception of the classification which he will follow in continuing the subject. Furthermore, it seems desirable, as early as possible, to urge that the discovery of the **periodic law**, which, in brief summation, characterizes the properties of all the elements as periodic functions of their atomic weights, constitutes one of the most material advances in chemical science.

In conclusion, we may state that the exact cause of this unmistakable natural relationship between certain groups of elements, is, at present, unknown. It is clearly recognized that the atoms themselves are not the ultimate particles of nature, but are more or less intricate aggregations of the much smaller *corpuscles*. (Cf.

Introduction, page 6.) Many authorities consider that a periodic similarity in the arrangement of corpuscles in the atom, causing a periodic similarity in properties, develops as the number of corpuscles, or the atomic weight, increases.

Interesting, in this connection, even to the beginner, are the simpler results of recent investigation on the subject by Professor J. J. Thompson (Cambridge). By considering a number of corpuscles all in one plane, and assuming that their tendency to fly apart due to their negative charges is balanced by an opposite force (positive sphere of electrification) acting everywhere inside the complex with equal intensity, thus constituting a stable arrangement, or atom, he is able to show mathematically that, as more corpuscles are added, there is a periodic similarity in the configurations which are stable under the influence of these forces. The mathematical development of this idea leads to a system of stable units resembling the periodic system in their relationship. Three dimensional arrangements, corresponding to the natural manifestation of matter, have proven too complicated for mathematical analysis, but there is reason to suppose that equally characteristic periodic relations would obtain.

## CHAPTER III.

### DETERMINATION OF MOLECULAR WEIGHTS.

If the correct formula of any compound is known, it is a comparatively simple matter to calculate its molecular weight by adding the constituent atomic weights, or such simple multiples of them as are specified in the formula. We have remarked that these atomic weights are very accurate relative numbers. Consequently, properly calculated molecular weights are very accurate relative numbers; in short, the numbers used in all practical calculations, which the chemist is called upon to perform.

Now, the approximate molecular weight of a substance may be determined experimentally quite aside from any previous knowledge with regard to its composition, and work of this sort constitutes the first step in developing the aggregate of accurate and indispensable information embodied in the atomic weight numbers and empirical formulas.

It is often true that the magnitude of a physical effect is determined by the numbers of molecules concerned in producing this effect, irrespective of their specific nature. Hence, the relative masses of different molecules may be deduced by comparative observations. We have already pointed out that equal numbers of molecules determine the same volume for all gases, if the temperature and pressure values are equal (Avogadro's Law). By comparing the masses of equal volumes of different gases under the same conditions of temperature and pressure, we obviously obtain the relation between their molecular masses—if one value is known, the other is thereby defined. Suppose *hydrogen* is adopted as the standard for such comparison. The density of a gas compared to hydrogen is obtained by dividing the weight of one volume of the gas by the weight of one volume of hydrogen, both gases measured under the same conditions:

Gas density (compared to hydrogen) =

$$\frac{\text{weight of 1 vol. gas}}{\text{weight of 1 vol. hyd.}} = \frac{\text{weight of 1 mol. gas}}{\text{weight of 1 mol. hyd.}}$$

But, one molecule of hydrogen contains two atoms (cf. Introduction, page 14) and must weigh twice as much as one atom of hydrogen. Therefore,

$$2 \times \text{Gas density} = \frac{\text{weight of 1 mol. gas}}{\text{weight of 1 atom hyd.}}$$

If the weight of one atom of hydrogen were taken as unity in our system of atomic and molecular weights, the second member of this equation would signify the molecular weight of the gas. However, we prefer to use **one sixteenth of the weight of the oxygen atom** as the unit standard in fixing these numbers. On this basis, the atomic weight of hydrogen is 1.0076, and the above equation may be altered thus:

$$2 \times 1.0076 \times \text{Gas density} = \frac{\text{weight of 1 mol. gas}}{\text{weight of 1 atom ox.} \div 16} =$$

#### Molecular weight of gas.

Calculations based on the simple gas laws give only approximate results (cf. Introduction, page 18); hence, the term 1.0076 is practically equivalent to unity in this connection, and we may write: *The (approximate) molecular weight of a gas is equal to twice its density compared to hydrogen.*

The density of a gas may be calculated from measurement of the volume containing a given weight of substance under carefully noted conditions, referred directly to hydrogen under these conditions, and then multiplied by two to give the molecular weight. In practice, no direct calculation of gas density is customary; the hydrogen comparison is omitted altogether, and a fundamental magnitude, called the **gram molecular volume**, is introduced. By this term, we understand the volume which includes one gram molecule (cf. Introduction, page 28) of a gas at 0° C., 760 mm. pressure. Since weights of different gases, which stand in the same proportion as their molecular weights, contain equal numbers of molecules (Relative numbers of molecules =  $\frac{\text{weight of one subst.}}{\text{its mol. weight}}$  and  $\frac{\text{weight of other subst.}}{\text{its mol. weight}}$ ) = 1 and 1, if the numerators of these expressions are propor-

tional to their denominators, as in above case), the volumes occupied by them, or more definitely, by single gram molecules of different gases under like conditions of temperature and pressure, are the same, according to the familiar *Law of Avogadro*. The value of this magnitude may be ascertained by measuring the volume occupied by 32 g. of oxygen (mol. weight of oxygen = 32, or twice 16, the atomic weight. Cf. Introduction, page 14) under the normal conditions noted above. It is approximately **22.4 liters**.

It should be clear, in view of the preceding discussion, that simple calculation of the weight of substance necessary to produce 22.4 liters of gaseous material at 0° C., 760 mm. pressure, results in a number, which can be none other than the **molecular weight of the substance**. We may, then, summarize the first method of molecular weight determination — applying only to substances which may be vaporized without decomposition — as follows: *Measure the volume occupied by a weighed quantity of the substance in gaseous form under convenient conditions. Reduce this volume to that corresponding to standard conditions by applying the simple gas laws and calculate the weight of material which will occupy 22.4 liters under these conditions.*

Problem: *Calculate the molecular weight of a substance, 2 g. of which furnish 395 c.c. of vapor at 100° C., 757 mm. pressure.*

$$\text{By Charles' Law, } 395 : x_1 :: 373 : 273 \\ \text{orig. vol.} \quad \text{altered vol.} \quad \text{orig. temp. (abs.)} \quad \text{final temp. (abs.)}$$

Whence,  $x = 289.1$  c.c. (vol. at 0° C., 757 mm. pressure).

$$\text{By Boyle's Law, } 289.1 : x_2 :: 760 : 757 \\ \text{altered vol.} \quad \text{final vol.} \quad \text{final press.} \quad \text{orig. press.}$$

Whence,  $x = 287.9$  c.c., or 0.288 l (vol. at 0°C., 760 mm. pressure).\*

Calculation of weight in gram molecular volume,

$$2 : x :: 0.288 : 22.4 \\ \text{orig. weight} \quad \text{weight in 22.4 l} \quad \text{vol. of 2 g}$$

Whence,  $x = 155.5$ , the molecular weight required.

\* Denoting the original values of pressure, volume and abs. temperature by  $p_0$ ,  $v_0$  and  $T_0$  and the final values by  $p_1$ ,  $v_1$  and  $T_1$ , the equation obtained by combining both laws reads:  $\frac{p_0 v_0}{T_0} = \frac{p_1 v_1}{T_1}$ . The final volume may thus be obtained by substituting the values given above in this equation and solving for  $v_1$ :  $\frac{(757)(395)}{373} = \frac{760 v_1}{273}$ .  $v_1 = 288$ .

The **molecular weights** of many substances which cannot be converted into gaseous material of the same kind, i.e., which decompose on heating, **may be deduced from quantitative observations on characteristic properties evidenced by their solutions in various solvents**. In other words, the number of dissolved particles determine the extent to which a certain property asserts itself. In considering these properties with respect to molecular weight determination, we must exclude aqueous solutions of acids, bases, and salts, since the particles present in such solutions are, in part, more elementary than molecules, and weights derived from reasoning along these lines cannot be correct molecular weights. (Discussion in Chapters VI and VII.)

It has been found that the particles of a substance as they exist dissolved in another substance, exert a pressure susceptible of measurement under certain conditions, which is in many ways to be compared with the pressure which a gas exerts against the walls of the containing vessel. This pressure is called **osmotic pressure** and will be discussed in a later chapter. For immediate purposes, it is sufficient to point out that the quantitative relations connecting osmotic pressure with the temperature and volume of the solution are precisely those existing between the pressure, temperature, and volume of a gas. Moreover, Avogadro's Law is equally prominent in this extended application: *Equal volumes of dilute solutions at the same temperature, contain the same numbers of ("dissolved") molecules, provided they possess the same osmotic pressure.*

Thus, it follows that the same reasoning adopted to ascertain the molecular weight of a substance in the gaseous state, may be applied to dissolved substances. The following procedure for determining the molecular weight of a dissolved substance, based on the application of the gas laws to dilute solution, is, in effect, a reiteration of that outlined above: *Measure the volume of solution containing a weighed amount of dissolved substance at the corresponding temperature, and determine the osmotic pressure. Calculate the weight of substance which would produce an osmotic pressure of 760 mm. when present in 22.4 liters solution at 0° C.*

Problem: *One gram of a compound dissolved in 246 c.c. solvent, gives an osmotic pressure of 800 mm. at 18° C. What is its molecular weight?*

$$\text{By Charles Law, } 246 : x_1 :: 291 : 273 \\ \text{orig. vol. altered vol. orig. temp. (abs.) final temp. (abs.)}$$

Whence,  $x = 230.8$  c.c. (vol. at 0° C., 800 mm. osmotic pressure).

$$\text{By Boyle's Law, } 230.8 : x_2 :: 760 : 800 \\ \text{altered vol. final vol. final osm. press. orig. osm. press.}$$

Whence,  $x = 242.9$  c.c. (vol. at 0° C., 760 mm. osmotic pressure).\*

Calculation of weight in gram molecular volume,

$$1 : x :: 0.243 : 22.4 \\ \text{orig. weight wt. diss. subst. vol. cont'g 1 g.} \\ \text{diss. subst. in 22.4 l diss. subst.}$$

Whence,  $x = 92.2$ , the molecular weight required.

A solution freezes at a lower temperature and boils at a higher temperature, i.e., possesses a lower vapor tension, than the pure solvent. The molecular weight of the dissolved substance may be calculated from measurements of the lowering of the freezing point, elevation of the boiling point, or vapor tension difference between solution and pure solvent. The mutual relationship between these three classes of phenomena is qualitatively indicated in the accompanying figure:

The curve  $ab$  represents the increase in the vapor tension of the pure solvent with the temperature. When a substance is dissolved in the solvent, the resulting solution has a lower vapor tension than the pure solvent, at all temperatures. This is indicated by the curve  $a'b'$ . Now, the pure solvent or the solution boils as soon as its vapor tension becomes equal to the atmospheric pressure  $P_1$ . In the case of the pure solvent, this occurs at the temperature  $T_1$ . At

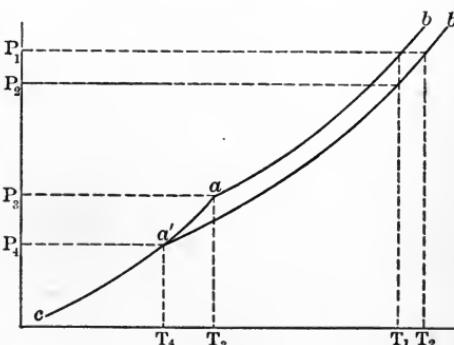


Fig. 2.

this temperature the solution has a lower vapor tension  $P_2$  than the atmospheric pressure  $P_1$ , hence it must be further heated—to the temperature  $T_2$ —before it will boil. Therefore, *to a lowering in vapor tension, there corresponds an elevation in boiling point.*

\* See note on page 49.

The curve  $ca$  represents the increase in vapor tension of the frozen solvent with the temperature. We may define the freezing point as that temperature at which the vapor tensions of both solid and liquid are equal. Only under this condition could the two states remain in contact with one another without tendency to change, as is the case at the freezing temperature. For the pure solvent, this temperature is  $T_3$ , the abscissa corresponding to the point ( $a$ ) where the vapor tension curves of liquid and solid intersect, i.e., where both solid and liquid have the same vapor tension ( $P_3$ ). When a solution is frozen, it is necessary that the pure solvent should appear as solid material, if the measurements are to be of value in molecular weight determination. This is generally the case, but not invariably so. Now, the curve  $a'b'$ , representing the vapor tensions of the solution, intersects the curve  $ca$ , representing vapor tensions of pure frozen solvent, at the point  $a'$ , the only point at which the vapor tensions ( $P_4$ ) of solid and liquid are equal. This point corresponds to the temperature  $T_4$  (less than  $T_3$ ), which is, consequently, the freezing point. Thus, we see that *a depression of the freezing point is determined by a lowering in the vapor tension of the liquid.*

Rigid quantitative connection between such associated properties of dilute solutions as we have cited, may be developed from theoretical considerations. If the osmotic pressure of a solution is known, it is quite possible to calculate the elevated temperature at which this solution will boil, its diminished vapor tension, or the depressed temperature at which it will freeze.

The method chosen for a specific molecular weight determination will obviously be that which presents the least experimental difficulty. Osmotic pressure measurements are difficult to perform, and yield comparatively inaccurate results. The freezing-point method is much more satisfactory in practice, and has been used extensively. A few additional remarks will serve to show how molecular weights are calculated from the results of freezing-point experiments.

As a basis for quantitative developments, in this connection, we have Raoult's Law, which states that *molecular quantities of different substances lower the freezing point of the same quantity of given solvent to the same extent.* Moreover, experiments show that

the lowering in any case increases in proportion as the concentration of the dissolved substance increases — that is, provided only very dilute solutions are considered. If "one gram molecule amounts" of different substances are dissolved separately in like quantities of solvent, the freezing-point depressions must be the same in all cases, according to this law. By adopting a definite amount of solvent to effect such solution we may define a characteristic constant applying to the use of this particular solvent. Thus, the depression (in degrees Centigrade) produced by one gram molecule of dissolved substance in 100 g. solvent is often called the **molecular depression**, or the **freezing-point constant of the solvent**. If a substance of known molecular weight is dissolved in this solvent, the constant may be calculated from available experimental data, and applied in calculating the molecular weights of other substances from data corresponding to their own solution in the solvent.

It remains to obtain a **mathematical expression** connecting the freezing-point constant with such direct experimental data:

Suppose we obtain a lowering of  $L^{\circ}$  C. by dissolving  $w$  grams of substance, possessing an (unknown) molecular weight  $M$  in  $W$  grams of a solvent, the freezing-point constant of which is  $K$ . This constant represents the lowering in 100 g. solvent, per gram molecule of dissolved substance, i.e.,

$$K = \frac{\text{lowering in } 100 \text{ g. solvent}}{\text{no. gram mols. diss. subst.}}$$

Since the lowering in  $W$  grams of solvent is  $L$ , the lowering in one gram of solvent produced by the same amount of dissolved substance will be  $LW$  (the concentration is  $W$  times as great), and the lowering in 100 grams of solvent will be  $\frac{LW}{100}$

(the concentration is  $\frac{1}{100}$  as great).

The actual weight of dissolved substance  $w$  divided by its molecular weight  $M$  gives the number of gram molecules of dissolved substance, viz.,  $\frac{w}{M}$ .

Substituting the expressions  $\frac{LW}{100}$  and  $\frac{w}{M}$  for the numerator

and denominator, respectively, in the right-hand member of the above equation, we obtain,

$$K = \frac{\frac{LW}{100}}{\frac{w}{M}}.$$

Clearing of fractions,  $K = \frac{LWM}{100w}$ , and transposing,  $M = \frac{100Kw}{LW}$ .

*Problem: Using 18.6 as the freezing-point constant of the solvent, calculate the molecular weight of the dissolved substance from the following data: grams solvent, 50; grams dissolved substance, 0.88; actual lowering, 0.95°.*

Substituting the values:  $W = 50$ ,  $w = 0.88$ ,  $L = 0.95^\circ$ , and  $K = 18.6$ , in the above equation, we obtain,

$$M = \frac{(100)(18.6)(0.88)}{(0.95)(50)}. \text{ Solving, } M = 34.5.$$

The calculation of molecular weights from boiling-point data involves the use of a formula similar to the above.

Additional methods of molecular weight determination are of relatively less importance than those described in this chapter.

## CHAPTER IV.

### DETERMINATION OF ATOMIC WEIGHTS.

SUPPOSE it has been found by experiment that about 76 g. of carbon disulphide occupy a volume of 22.4 liters at 0° C., 760 mm. pressure. We know, then, that a molecule of this substance weighs approximately 76 times as much as the unit quantity of material adopted as a basis of comparison for all atomic and molecular weights, namely, the sixteenth part of the oxygen atom. In other words, its molecular weight is approximately 44.

Now, it is always possible, by some quantitative method of chemical analysis, to determine the exact proportions by weight in which the individual constituents are present in a compound. Thus, we are able to divide the molecular weight unit into parts representing the weights of its several constituents. Such analytical methods are sometimes direct, more often indirect, and involve the use of much cumulative data relative to the composition and particular behavior of certain substances. If a weighed quantity of carbon disulphide could be decomposed into its elements, and these, in turn, weighed, we would possess the results of a direct analysis. By burning a weighed quantity of carbon disulphide and weighing the resulting carbon dioxide, after rendering it suitably pure, we would obtain indirect results leading to the composition of the material. Thus, previous experiment has shown that 27.3 + per cent of the material in carbon dioxide is carbon — by direct synthesis, 27.3 + parts of carbon unite with 72.7 — parts of oxygen to form 100 parts carbon dioxide — and it is only necessary to multiply the weight of carbon dioxide obtained from our initial quantity of carbon disulphide by this percentage number, to ascertain how much carbon the latter originally contained. The complementary

amount of sulphur is obtained by difference — original weight of carbon disulphide minus weight of carbon — since the compound is known to contain no third constituent.

Analysis of the compound, carbon disulphide, shows that 15.8 per cent of its total substance is carbon, while the remainder, 84.2 per cent, is sulphur. In the preliminary discussion (cf. Introduction, page 22, in particular) we have already demonstrated that a molecular weight combines the atomic weights, or multiple atomic weights of such elementary substances as compose the compound. Consequently, 15.8 per cent of  $76 = 12.0$  (that part of the molecular weight of carbon disulphide attributable to carbon) must be the (approximate) simple or multiple atomic weight of carbon; and 84.2 per cent of  $76 = 64$  (that part of its molecular weight attributable to sulphur) must be the (approximate) simple or multiple atomic weight of sulphur.

It is clear that an extension of this line of work to a large number of compounds containing carbon, will result in a series of numbers representing either the atomic weight of carbon, or multiples of the same, and furthermore, that the simple number is reasonably certain to develop if the number of compounds investigated is very great; i.e., some one of these compounds will, in all probability, contain a single atom of carbon in its molecule. The determination of other atomic weights is effected by a similar course of procedure.

The following outlined arrangement serves to briefly summarize this argument.

#### To Determine the Approximate Atomic Weight of an Element:

- (1) *A table of the molecular weights of a large number of compounds containing the element is prepared.*
- (2) *The compounds are analyzed and that portion of the molecular weight consisting of the element under consideration, is tabulated along with the corresponding molecular weight.*
- (3) *The smallest of these latter numbers is chosen as the atomic weight sought, for larger numbers evidently represent more than one atom, and are consequently multiples of the correct atomic weight.*

To illustrate:

Carbon.				Sulphur.			
Compound.	Mol. Wt.	Per cent C. in Comp'd.	Part of Mol. Wt. Consisting of C.	Compound.	Mol. Wt.	Per cent S. in Comp'd.	Part of Mol. Wt. Consisting of S.
Carbon monoxide	28	42.9	12	Sulphur dioxide	64	50.0	32
Carbon dioxide ....	44	27.3	12	Sulphur tri-oxide	80	40.0	32
Carbon di-sulphide ..	76	15.8	12	Carbon di-sulphide	76	84.2	64
Methane....	16	75.0	12	Hydrogen sulphide	34	94.1	32
Acetylene ..	26	92.3	24	Sulphuryl chloride	135	23.7	32
Benzene.... etc.	78	92.3	72	Sulphur etc.....	64	100.0	64

From these two tables, we choose the values 12 and 32 as the atomic weights of **carbon** and **sulphur**, respectively.

It is obviously of great importance to be able to verify an atomic weight number, selected as above, by some independent method. Such a check is offered by the **Law of Dulong and Petit** (Paris, 1818):

*The products of the atomic weights of the elements into their specific heats are approximately constant.*

The mean value of this product is 6.4. We should note that the specific heat of an element varies with the temperature; in some cases, very emphatically. Moreover, not a few of the elements are polymorphous (cf. Introduction, p. 16), in which case each solid modification has its own characteristic specific heat. Some elements do not follow the law very closely. Nevertheless, deductions from this source are of service, in a broad sense, to indicate whether the atomic weight number resulting from chemical reasoning (as above), is a minimum value, or still a multiple of the true value. The fact that conclusions from both sources are quite generally in accord, justifies an increased confidence in their accuracy.

Additional evidence tending to establish the general accuracy of these numbers, is offered by the **Periodic System** (Chapter II). The very realization of a comprehensive classification of this sort based on this series of numbers, testifies to their significant nature. Indeed, when sufficiently elaborate chemical data to fully establish the atomic weight of an element are not available, its logical position in the periodic system may be depended upon to suggest the order of this number.

We have seen how an approximate number is chosen for the atomic weight of an element. The greater number of atomic weights are now known accurately to one or two places of decimals. This refinement is based on very careful analytical work, showing, as accurately as possible, the ratios by weight characterizing combination between the different elements and oxygen. It is not necessary to determine the combining ratio between every element and oxygen directly — some elements fail to combine with oxygen, or form oxides which are unsuited to analysis — since this ratio may be calculated if the data relative to combination with another element, as well as the oxygen ratio of this other element, is known. To obtain a uniform comparison with the arbitrary standard  $O = 16$  the oxygen term of the ratio is altered to exactly 16, and the other term recalculated on this basis. The resulting number may then require to be multiplied, or divided by some simple integer to furnish the correct atomic weight, already known in approximation.

It should be clear that the combining ratio between the element and oxygen — perhaps ascertained indirectly — may represent a relation between any small number of atomic quantities of the element and any small number of atomic quantities of oxygen. In any case, the weight of element is finally referred to one atomic quantity of oxygen, and may, thus, constitute a simple fractional part, or multiple, of the atomic weight. Since we know the approximate atomic weight from previous considerations, it is at once apparent how this number must be altered to yield the accurate atomic weight.

An example will serve to further elucidate these statements:

By the process outlined on page 56, the "round number" atomic weight of hydrogen is fixed at 1.

Unusually elaborate and extended experiments have placed the ratio of hydrogen to oxygen in the compound, water, at  $0.12595 \pm 4 : 1$ . Changing the oxygen term to 16, the ratio becomes,  $2.0152 : 16$ . Since the approximate atomic weight of hydrogen is 1, the number 2.0153 divided by 2, gives the refined atomic weight value, — 1.0076. The particular significance of the multiple number is that *two* atoms of hydrogen are combined with *one* atom of oxygen in the above compound.

The atomic weight most frequently used in chemical calculations is that of oxygen. It is, therefore, desirable in standardizing these relative weights that some convenient whole number should be adjusted to oxygen. Berzelius proposed regulation of these numbers on the basis of O = 100. This standard has not met with general approval. On the other hand, hydrogen possesses the smallest atomic weight of any known element and might logically be adopted as unity. In such event, the oxygen number would be a trifle under 16, — a rather inconvenient fractional value. It has proven most uniformly satisfactory to make this number exactly 16 (the value which we have used in earlier portions of this text). On this basis, the atomic weight of hydrogen becomes 1.0076 (as shown in the previous paragraph); a number so close to unity that the decimal part need not be considered in practical work. Other atomic weights are invariably referred to this standard, whereby they assume values which are only infrequently expressed by whole numbers.

We may sum up the essential features of the preceding remarks in the form of a rigid **definition of the term atomic weight:** *An atomic weight is a number expressing the ratio of the mass of the smallest part of an element entering into combination, to  $\frac{1}{16}$  of the mass of an atom of oxygen.* An international commission critically examines all new experimental work in this field and revises the list of atomic weights each year. The 1908 Table is to be found inside the cover of this book.

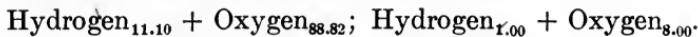
## CHAPTER V.

### CALCULATION OF FORMULAS.

WE have seen that a **formula** specifies the number of atomic quantities of each elementary substance which together constitute one molecular quantity of the compound. Consequently, the composition of a compound must be determined by some process of analysis before any calculation relative to numbers of different atoms in a molecule is possible. The results of chemical analysis are usually presented in such a way that the proportion of each constituent appears as a percentage of the whole. If the analysis is correct, these percentage numbers should total 100, within the limits of experimental accuracy. Thus, a satisfactory analysis of the compound *water* would be:

Hydrogen .....	11.10 per cent (by weight)
Oxygen.....	88.82 per cent
Total .....	99.92 per cent.

The analysis might be referred to one part by weight of hydrogen. Either of the following expressions, in which the figures denote *parts by weight*, describes the results of this analysis:



Now, if we are to use symbols, and assemble our data in the shape of a formula, we must observe that each symbol stands for a certain weight of its particular kind of matter, called the atomic weight. Hence, the relative atomic proportions of hydrogen and oxygen in the compound *water* obtained by dividing the actual proportions by weight by the respective atomic weights ( $H = 1$ ,  $O = 16$ ), may be associated with the symbols, thus:

$$\begin{array}{ccc} \text{H}_{11.10} \text{ O}_{5.55} & : & \text{H}_{1.00} \text{ O}_{0.50} \\ \left( \frac{11.10}{1} = 11.10, \text{ and } \frac{5.55}{16} = 0.50 \right) & : & \left( \frac{1.00}{1} = 1.00, \text{ and } \frac{0.50}{16} = 0.50 \right) \end{array}$$

At this point, we should reflect that a formula must represent the **actual numbers of different atoms which constitute one molecule of the substance**. Moreover, these numbers must be simple integers, since one atom is the smallest unit concerned in chemical combination. If, in the above ratio, we assume one atom of oxygen, there will result an integral number of hydrogen atoms, namely, two. But no evidence has been introduced, thus far, to prove that a molecule of water does not contain two atoms of oxygen and four of hydrogen, or some larger total of oxygen and hydrogen atoms, always in the proportion one to two. Therefore, at this stage we may write the simple formula  $H_2O$  with the understanding that it is to a certain extent hypothetical; or the general formula  $H_{2n}O_n$  in which  $n$  is some simple integer.

This uncertainty is removed through an actual determination of the molecular weight. The molecular weight of water, if its formula is  $H_2O$ , must be 18, i.e.,  $((2 \times 1) + 16)$ . An experimental determination of the molecular weight by the gas density method (cf. Chapter III) presents no difficulty in this case, and results in the above value. Hence, we accept the formula  $H_2O$  without question, as descriptive of the compound *water*. Had a multiple of 18 been obtained in the molecular weight determination, corresponding alteration of the simple formula would have been necessary, in order to secure the proper agreement. Thus:

Molecular Weight.	Formula.
18.....	$H_2O$
36.....	$H_4O_2$
54.....	$H_6O_3$
$18 n$ .....	$H_{2n}O_n$

A working summary of the preceding argument is embodied in the following **Rule for the Calculation of Formulas**: *Divide the numbers which represent the relative weights of each element in the compound, by the corresponding atomic weights. The resulting series of numbers represents the numerical proportionality between the several kinds of atoms in the molecule. Assign the value 1 to the smallest of these numbers and recalculate the others on this basis. Construct a formula using these recalculated num-*

bers (which should be simple integers) as subscripts, and compare the molecular weight corresponding to this formula with the experimentally determined molecular weight. If substantial agreement is apparent, this simplest formula meets all requirements. Otherwise, to obtain a correct formula, divide the experimentally determined molecular weight by the molecular weight calculated from the simplest formula, and multiply each subscript in this formula by the quotient, which must approximate a simple integer.

Illustrative calculations:

**Sulphur Dioxide:**

	Percentage Comp.		At. Wts.		At. Ratio.	Simplest Ratio.	Mol. Wt. from Gas. D.
Sulphur.....	50.05	÷	32.06	=	1.56	1.00	
Oxygen.....	49.95	÷	16.00	=	3.12	2.00	
	100.00						About 64

**Rational Formula,  $\text{SO}_2$ :** — The simplest formula suggested by the numbers in the fourth column above is  $\text{SO}_2$ . The molecular weight corresponding to this formula is  $64.06$  ( $32.06 + (2 \times 16)$ ), in substantial agreement with the above value, 64. (All the above numbers are *ideal*, for purposes of illustration.)

Sometimes it is desirable to express the results of an analysis in terms of characteristic groups of atoms. The analytical data in the following table relates to a very pure sample of the mineral, gypsum.\*

	Percentage Comp.		Formula Wts. of Constituents.		Ratio.	Simplest Ratio.
$\text{H}_2\text{O}$ .....	20.85	÷	18.02	=	1.16	2.03
$\text{CaO}$ .....	32.84	÷	56.1	=	0.58	1.02
$\text{SO}_3$ .....	46.07	÷	80.06	=	0.57	1.00
	99.76					

**Simplest Formula,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ :** — The simplest formula corresponding to these results is  $\text{CaO} \cdot \text{SO}_3 \cdot 2\text{H}_2\text{O}$ , or  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ .

\* Analysis by a student in the Sheffield Scientific School.

In this case, no molecular weight determination is available for further criticism.

The reference literature of Chemistry is essentially a collection of definite chemical information relative to all known substances, in which their formulas occupy a prominent position. For the most part, simplest formulas (according to previous interpretation) figure in the general enumeration. The simplest formula corresponds to the correct molecular weight in the majority of investigated cases. It should be noted, however, that the molecular weights of many compounds have never been determined. Consequently, the simple formulas assigned to them, while certifying to their composition, may or may not represent their molecular weights.

The ordinary methods of molecular weight determination deal with a substance in the gaseous or dissolved state. There is, perhaps, a general tendency for the same substance to persist in a definite molecular condition throughout change from one to the other of these states. Nevertheless, many exceptions may be noted — indeed, change in molecular complexity in the gaseous state alone, frequently accompanies change of temperature. No method of determining the molecular weight of a solid is known.

Immediate knowledge of the formulas pertaining to many important compounds is preëminently valuable to the student of Chemistry. Fortunately, a comprehensive array of analogies and relationships underlies the whole scheme of chemical combination, rendering a minimum amount of well chosen data directly available for predicting a wealth of detailed information. Any ordinary formula is readily constructed by adjusting its **individual constituent parts** according to certain well recognized principles of equivalence, which have resulted from the critical examination of many other formulas (cf. Introduction, page 23). This is, in no sense, a rigid determination, or calculation of the formula, but rather an empirical method of rendering our knowledge systematic and helpful.

## CHAPTER VI.

### OSMOTIC PRESSURE AND RELATED PHENOMENA, WITH PARTICULAR REFERENCE TO DILUTE AQUEOUS SOLUTIONS OF ACIDS, BASES, AND SALTS.

In a previous chapter, we have noted that the dissolved particles of a solution give rise to a certain pressure effect which obeys the same laws as that due to the particles of a gas. For purposes of comparison, it may be imagined that total elimination of the solvent would convert the dissolved particles into a like number of gaseous particles exerting **gaseous pressure** equal in magnitude to the **osmotic pressure**, which they determined when in the dissolved condition. Gaseous pressure is apparent at the bounding surfaces of the gas. On the other hand, the pressure on the walls and bottom of a vessel containing a solution is purely gravitational in nature. The marked difference between the properties of a gas and those of a liquid explains this non-conformity in the manifestation of gaseous pressure and osmotic pressure. Forces of great magnitude are concerned in restraining the particles of a liquid from realizing their inherent disruptive tendency. Outside pressure is not necessary to limit the volume occupied by matter in this state of aggregation, since a self-imposed surface characterizes the liquid state. The forces operating at such a liquid surface determine a pressure effect directed towards the interior of the liquid, at right angles to the surface, i.e., in direct opposition to the osmotic pressure. Experimental study of surface tension phenomena has led to a quantitative estimate of such surface pressures. It appears that they vastly exceed any possible osmotic pressure. Consequently, the latter effect will not appear at a free surface.

To measure the osmotic pressure of a dissolved substance, we must, therefore, eliminate the free surface. This is accomplished by arranging a boundary between the solution in question and an amount of pure solvent, which shall permit ready passage of

the solvent in both directions, but completely enclose the dissolved particles. Thus, we experiment in a medium of pure solvent, which pervades the whole system. Membranes composed of copper ferrocyanide, or certain other gelatinous bodies, are permeable to water and impermeable to most dissolved substances. In this connection, they are called *semi-permeable membranes*. The cellular tissue of plants and animals is semi-permeable with respect to aqueous solutions of various compounds, and osmotic phenomena are prominently concerned in its natural functions.

Suppose the cylinder represented in Fig. 3 contains a solution of sugar in water, separated from a quantity of pure solvent by a partition, which permits unrestricted passage of the water, but is impervious to the sugar molecules. There is no surface to mark the division between these two compartments, since water is continuous throughout the whole system. Under these conditions, the osmotic pressure due to the sugar molecules contained in the lower compartment will be apparent at the partition, and may be measured indirectly, as we shall see later. If the partition is movable, it will be forced upwards through the pure water until the osmotic pressure of the solution, which decreases as water enters, becomes just equal to the task of supporting its weight. In case no partition had prevented the dissolved particles from escaping, they would have penetrated the pure solvent until the osmotic pressure had become equal throughout the whole solution. In other words, *diffusion* would have proceeded until a uniform concentration had obtained.

Owing to the delicate nature of these semi-permeable membranes, their practical use in furthering the measurement of osmotic pressure is dependent on some arrangement calculated to render them sufficiently rigid. According to the method commonly used, they are supported by the walls of a porous earthenware vessel. Solutions which will precipitate the membrane by interaction, are allowed to penetrate the walls of the vessel from either side, thus meeting in the interior and depositing

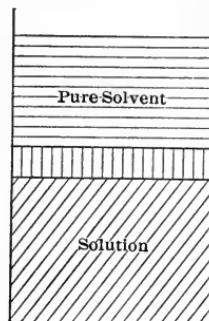


Fig. 3.

a thin membrane, which is rigidly secured by the wall substance. Reinforced copper ferrocyanide membranes of this sort are capable of withstanding osmotic pressures of several atmospheres. No membranes of sufficient rigidity to permit accurate work with rather concentrated solutions (in which the osmotic pressure may exceed 100 atmospheres) have been constructed.

A clear conception of the actual process employed to determine the osmotic pressure of a solution is best obtained with the help of the accompanying diagram (Fig. 4). The porous cup *C* is prepared for the experiments by depositing a membrane of copper ferrocyanide within its wall substance. It is then

fitted with a stopper carrying a long glass tube, and filled to the bottom of the stopper with the solution to be investigated. This apparatus is immersed in a bath of pure solvent *S* to a depth which brings both liquid surfaces to the same level. The particles of dissolved substance exert a pressure on the membrane. This is held by the cell walls and cannot yield.

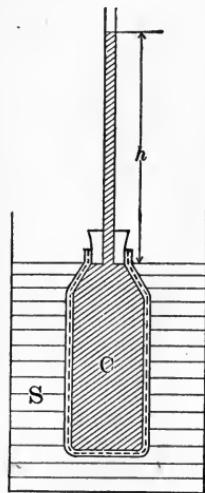


Fig. 4

Now, any system invariably tends to such readjustment as will operate against an imposed deformation. A flow of solvent through the membrane into the solution, whereby the solution becomes diluted and its osmotic pressure diminished, therefore ensues. The resulting increase in the volume of the solution causes it to rise in the tube, and this effect persists until the hydrostatic pressure of the liquid column (*h*) exactly balances the tendency to inflow. Since the magnitude of this inflow effect is determined by the osmotic pressure of the original solution — its cause — the resulting hydrostatic pressure, measured by the height of the column (*h*), is equal to the osmotic pressure.

We have accounted for gaseous pressure by picturing rapid motion of the constituent molecules, resulting in countless impacts against the walls of the containing vessel. This explains all facts well and is generally acceptable to the scientific fraternity. To associate osmotic pressure with gas pressure, we have con-

ceived the space between the molecules of a gas to be filled with solvent. But, whether a similar kinetic hypothesis, or some other hypothesis, such as the assumption of attractive forces between dissolved substance and solvent, offers the most rational explanation of osmotic pressure, is an open question.

In the course of our discussion relative to the determination of molecular weights, we noted the failure of methods employing dilute solutions to yield the correct molecular weight when the dissolved substance is an acid, base, or salt; and the solvent, water. It is just such solutions which merit especial interest on the part of the chemist, by reason of their commonplace occurrence. Consideration of some typical results obtained by the application of these methods to such solutions will be of value in introducing certain fundamental ideas as to the nature of dissolved substances in general.

For this purpose, we may choose the **freezing-point method** in preference to the **osmotic pressure method**, chiefly because it presents less experimental difficulty and has received more attention. The close relationship between these different properties of solutions has already been pointed out (cf. Chapter III).

From previous considerations, we would expect one gram molecule of *sodium chloride* to produce the same freezing-point lowering in a liter of water as one gram molecule of *sugar*, or any other dissolved substance does. That is, as many molecules are dissolved in each case, and we have seen that it is the number of molecules which determines the magnitude of the lowering. In reality, the *salt* is much more effective in this respect. Thus:

Lowering in 1000 g. water by 1 g. mol. (342 g.) cane sugar	1.86°
Lowering in 1000 g. water by 1 g. mol. (58.5 g.) salt.....	3.46°.

Since the lowering is proportional to the number of molecules, or concrete particles in general, we reason that the *salt solution* contains  $\frac{3.46}{1.86}$ , or 1.86 times as many particles as the *sugar solution*.

If we consider the figures given by *sugar* (and duplicated by other substances which are not acids, bases, or salts) as normal, then we may place the normal *freezing-point constant* of water at 18.6, i.e., the lowering produced by one gram molecule of dissolved substance in 100 grams of solvent (cf. Chapter

III, page 53). Using this value in the formula  $M = \frac{100 Kw}{LW}$

in connection with the actual lowering produced by 58.5 g. *salt* in 1000 g. water— $3.46^\circ$ —we calculate the molecular weight of *salt* to be 31.4. Now, it is certain that the formula of common *salt* is NaCl, and its molecular weight, 58.5. Hence, the above result indicates that the (average) formula weight of the particles present in the aqueous solution of salt—31.4—is less than the true molecular weight. We are forced to the general conclusion that the process of solution has caused some sort of disruption, or dissociation (since *salt* is again formed on evaporation) of the original *salt* molecules into smaller parts, each of which is comparable with a whole molecule in its power to lower the freezing point of the solvent.

The following reasoning suffices to show what proportion of the molecules have suffered alteration: At the outset we will make the assumption that each molecule which dissociates, furnishes two particles. Theory concerning the nature of these particles is introduced in the next chapter. At this point, we need only state that a molecule consisting of one atom of *sodium* and one atom of *chlorine* could scarcely be expected to furnish more than two concrete chemical particles of any sort.

Let  $(m)$  equal the fractional part of molecules which dissociate. Then  $(1 - m)$  will represent the fractional part of molecules which fail to dissociate, and  $2m + (1 - m)$ , or  $(1 + m)$ , the total number of particles (molecules and portions of molecules) present in the solution for every original molecule dissolved. But, we have seen above that the solution contains 1.86 times as many particles as the *sugar* solution, and we dissolved the same number of molecules in each case. Therefore, 1.86 particles are present for every molecule dissolved and we write,  $(1 + m) = 1.86$ . Whence,  $(m) = 0.86$ . This number signifies that 86 per cent of the *salt* molecules in a solution containing 58.5 grams of *salt* per liter of water, are dissociated into two parts.

## CHAPTER VII.

### THE ELECTROLYTIC DISSOCIATION THEORY.

As a basis for the **formulation of a theory which shall explain the condition of substances in solution**, we have these fundamental facts to consider:

(1) Those substances, and only those, which conduct the galvanic current in aqueous solution, give rise to greater osmotic pressure, etc., in the same aqueous medium, than is calculated from their molecular weights in the usual way (by application of Avogadro's Law).

(2) These substances do not show this abnormality when dissolved in most other solvents, and such solutions do not conduct the current to any great extent.

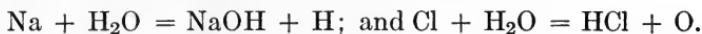
(3) Chemical reactions of a particularly significant character are associated with the aqueous solutions of these substances.

We remarked briefly on the chemical nature of these compounds in the earlier discussion of their abnormally pronounced effect in lowering the freezing point of water. Attention is again directed to the fact that they include the three great classes of compounds which are most representative of the whole chemical fabric — *acids*, *bases*, and *salts*. The term, **electrolyte**, is employed to designate all of these substances, with reference to their ability to conduct the galvanic current, when in a suitable condition, such as that of solution in water.

Substances which do not conduct the galvanic current in aqueous solution, or **non-electrolytes**, are supposed to disintegrate into molecules when dissolved in any liquid. We have seen (Chapter III) how careful consideration of the properties of their solutions leads consistently to this conclusion. But, the aqueous solution of an electrolyte contains more particles than would correspond to a division into simple molecules. It was suggested at the close of the previous chapter, that this condition could be explained by assuming a kind of dissociation in the aqueous solution, whereby some of the molecules of the dis-

solved substance furnish two or more particles. This reasoning was carried far enough to show how the numerical proportion of molecules which dissociate, could be calculated by comparing the actual freezing-point lowering with the normal lowering in a solution of the same molecular concentration.

There remains the necessity of placing this theory on a practical footing by introducing some logical conception of the **nature of these sub-molecular particles**. Reverting to the specific case previously considered, it is not reasonable to suppose that *sodium chloride*, NaCl, when dissolved in water, dissociates into concrete particles, or atoms, of *sodium* and *chlorine*; for we know that both these substances in the atomic state react chemically on water, forming other products. Thus:



The modified conception, which renders a primary assumption of simple dissociation tenable in the face of all requirements, is embodied in the **Electrolytic Dissociation Theory**, proposed by **Arrhenius** (Stockholm, 1887). In effect, **each particle is supposed to carry a certain quantity of electricity, which thus materially changes its nature**. This appears quite reasonable if we reflect that it is the association of matter with energy which determines the nature of chemical, as well as physical change — the association of an electric charge with the sodium atom might well prevent it from reacting with water, as above. Positive and negative electricity cannot appear independently. Consequently, the dissociation products from each molecule will be of two kinds, i.e., those carrying positive charges, and those carrying complementary negative charges.

**Electrolytic dissociation** follows a plan suggested by general chemical reaction. Thus, the compound *potassium chlorate*,  $\text{KClO}_3$ , dissociates into positive — K — particles and negative —  $\text{ClO}_3$  — particles, and the integrity of the —  $\text{ClO}_3$  — particle is generally preserved throughout diverse chemical reaction. The name, *ion* (positive or negative, respectively), is applied to a particle of this sort, and the process by which ions are formed (attending solution of an electrolyte in water for example) is called *electrolytic dissociation*, or *ionization*. An ion which corresponds to the chemical valence 1 carries a unit charge. This is

represented by entering one (+) over the symbol, or group of symbols describing its identity. A bivalent atom or group produces an ion of double charge (++) , etc. The whole valence scheme serves as a key to the distribution of these ionic charges. A few illustrations will make this matter clear:

One molecule of *sodium chloride* NaCl gives one *sodium ion* with unit positive charge, represented — $\overset{+}{\text{Na}}$ , and one *chloride ion* with unit negative charge, represented — $\bar{\text{Cl}}$ .

One molecule of *sodium sulphate*,  $\text{Na}_2\text{SO}_4$ , gives  $2\overset{+}{\text{Na}} + \overset{+-}{\text{SO}_4}$ .

One molecule of *barium chloride*,  $\text{BaCl}_2$ , gives  $\overset{++}{\text{Ba}} + 2\overset{-}{\text{Cl}}$ .

One molecule of *cupric nitrate*,  $\text{Cu}(\text{NO}_3)_2$ , gives  $\overset{++}{\text{Cu}} + 2\overset{-}{\text{NO}_3}$ .

One molecule of *lead acetate*,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ , gives  $\overset{++}{\text{Pb}} + 2\overset{-}{\text{C}_2\text{H}_3\text{O}_2}$ .

One molecule of *nitric acid*,  $\text{HNO}_3$ , gives  $\overset{+}{\text{H}} + \overset{-}{\text{NO}_3}$ .

One molecule of *sodium hydroxide*,  $\text{NaOH}$ , gives  $\overset{+}{\text{Na}} + \overset{-}{\text{OH}}$ .

While the general idea of dissociation included in our theoretical conceptions relative to aqueous solutions of electrolytes, is definitely suggested by the abnormal behavior of these solutions (as previously shown), consideration of the actual phenomena associated with the conduction of electricity by such solutions has contributed most effectively towards maturing this theory. The prospect of a much clearer insight into the essential assertions of the Electrolytic Dissociation Theory, will justify the use of some space for a detailed description of such phenomena, viewed from this standpoint. Before turning to a specific case, it is especially desirable to state with all possible emphasis, that the passage of electricity through an aqueous solution of an electrolyte is accompanied by an alteration in the chemical nature of the material; a transfer of matter differentiates **electrolytic conduction**, or conduction of the second class, from **metallic conduction**, or conduction of the first class, during which no material change occurs. The process of decomposition, attending the passage of electricity through a substance, or mixture, is called **electrolysis**. To avoid misconception on the part of the reader, we should note here, that electrolysis is not

confined to aqueous solutions of electrolytes, although dependent on the presence of ions. Some other solvents produce the same ionic condition in an electrolyte. *Water* is by far most effective in this respect, however. Again, a pure electrolyte may become quite conductive at high temperatures. Thus, we refer to the **electrolysis of certain non-aqueous solutions and of fused electrolytes.**

Let us consider the electrolysis of a dilute solution of *hydrochloric acid in water*: If no acid were dissolved in the water, the latter would scarcely conduct at all. Likewise, if pure acid were used, very slight conductivity would result. But the solution contains particles not present to any appreciable extent in either pure substance, namely, *hydrogen ions* and *chloride ions*. These particles are thought to transport electricity from pole to pole. Each dissociating molecule of acid furnishes one *hydrogen ion*, carrying a unit positive charge, and one *chloride ion*, carrying a unit negative charge. If the solution is very dilute, most of the acid molecules are dissociated, so that an almost endless number of charged particles are present. It is obvious that no apparent electrification of the solution will result, since there can be no excess of one kind of electricity over the other. The process of dissolving acid in water has, in some obscure manner, caused a readjustment of energy within the system, especially characterized by the appearance of sub-molecular fragments, which are possessed of electrical energy, operating to prevent their complete alienation, i.e., there is a reciprocal attraction between complementary fragments carrying equal and opposite charges of electricity.

Suppose we follow the process of alteration which a tangible number of these dissociated acid molecules may be expected to sustain when suitable electrodes\* connected with some outside source of electricity are introduced into the solution in which they are contained. Four such dissociated molecules are shown underneath the lowest dotted line in Fig. 5. The heavy lines *A* and *C* represent platinum plates which are connected with a dynamo, or other apparatus for generating electricity.

\* Platinum electrodes are commonly used in experiments of this sort, owing to their general resistance to corrosion. In this particular case, however, platinum would not remain unattacked and carbon is a more suitable electrode material.

Electrical generators cause a separation of positive from negative electricity by mechanical agency. The positive electricity is accumulated in one part of the apparatus, and the negative electricity in another part. Between these two regions there exists a difference in *potential*, or electrical pressure, corresponding to the attractive force between positive and negative electricity. If regions of high and low potential are joined by a metallic conductor, an electric current flows until equalization of the potential is effected. The generator maintains a constant difference of potential, and therefore determines a continuous current.

For immediate purposes we will assume that the positive pole or electrode, called the *anode*, is charged with a definite amount of electricity, conveniently measurable in terms of the unit quantity

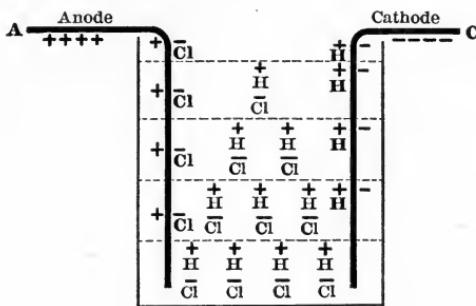


Fig. 5.

associated with one hydrogen ion, and that the negative pole or *cathode* is charged with an equal amount of negative electricity.

The small plus and minus signs arranged along the anode and cathode, respectively, indicate the magnitude of these charges. Now, the relatively large quantity of positive electricity at the anode will exert an attractive force on the nearest negative ion — called *anion*, in this connection — and a repulsive force on its positive fellow, sufficient in effect to overcome their mutual attraction. Simultaneously, negative electricity at the cathode attracts the nearest positive ion — *cation* — and repels the accompanying negative ion. All the particles are supposed to be moving about in the solvent medium; consequently, the positive ion and negative ion which were repelled towards the interior of the liquid will sooner or later come close enough together so that their reciprocal attraction will determine close

partnership between them. The negative ion which was attracted by the anode will lose its charge when it reaches this locality, owing to neutralization of the same by an equal amount of positive electricity. After the loss of its negative charge, this *chlorine atom* possesses the ordinary chemical properties of *atomic chlorine*. According to conditions of concentration, temperature, etc., it may unite with another *chlorine atom* to form a molecule of *gaseous chlorine*, which will be liberated, or it may react with *water* to form *oxygen*, which will be liberated in the molecular condition:  $\text{Cl} + \text{H}_2\text{O} = 2\text{HCl} + \text{O}$ , and  $\text{O} + \text{O} = \text{O}_2$ .\* The positive ion which was attracted to the cathode, will lose its charge by neutralization, ultimately appearing as *molecular hydrogen*.

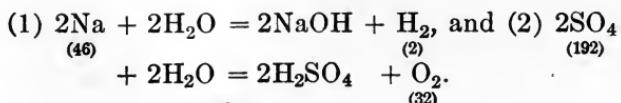
Conditions subsequent to the process just described, are represented in that part of the figure immediately above the lower dotted line. There are now three undecomposed molecules of *hydrochloric acid*, in the ionic form. Symbols printed in bold type indicate the elements in their ordinary atomic condition. Plus and minus signs arranged side by side are to be regarded as extinguishing one another. We see that the production of one atom of *hydrogen* and one atom of *chlorine* is identified with the loss of one negative unit of electricity from the cathode and one positive unit from the anode. The continuation of this process is outlined by upward steps in the figure. Ultimately, all four molecules of acid are decomposed at the expense of four units of positive electricity and four units of negative electricity. Instead of the eight units originally present on the anode and the eight originally present on the cathode, four units are finally left at each place. This evidently corresponds to the direct passage of four positive units from the anode to the cathode. In practice, the generating apparatus supplies these amounts of electricity as fast as they are used, i.e., maintains a constant difference of potential, and a measuring instrument inserted anywhere within the circuit shows the quantity of electricity passing.

By determining the **quantity of electricity** which flows through the circuit in a definite time interval, as well as the **actual weight of hydrogen** liberated during the same time, we are

\* Concentrated solutions yield  $\text{Cl}_2$  for the most part; dilute solutions yield  $\text{O}_2$ .

in a position to ascertain how much electricity has been carried by an ionic quantity of *hydrogen*, or by an ionic quantity of *chlorine*. (The term, *ionic quantity*, will be understood by comparing the analogous terms, *atomic quantity*, and *molecular quantity*.) Thus, experiment shows that **one gram ion of hydrogen** (formula weight of the ion expressed in grams), or one gram of *hydrogen*, is liberated every time **96,500 coulombs\*** of electricity traverse the circuit. It is clear, in view of the above discussion, that the apparent transfer of 96,500 coulombs from *A* to *C* (Fig. 5) was brought about by one gram ion of *hydrogen* (which carried this amount of positive electricity to *C*), in common with one gram ion of *chlorine* (which removed this amount of positive electricity from *A*, in that it carried an equal amount of negative electricity to this region). Hence, we conclude that one gram ion of *hydrogen* (1 g.) carries a positive charge of 96,500 coulombs, and one gram ion of *chlorine* (36.45 g.) carries a negative charge equal in amount.

We have stated (on page 71) as an essential precept of the *Electrolytic Dissociation Theory*, that the ordinary chemical valence of an atom or group indicates the number of unit electrical charges it will carry as an ion. Referring to the table on page 71, we have only to substitute 96,500 coulombs for each single plus or minus to ascertain the magnitude of the charge carried by any one of the ions enumerated. It is equally simple to determine what quantity of a given ion will be liberated during electrolysis. For, obviously, the passage of 96,590 coulombs through the medium in which it is contained, will liberate one gram ion, if it carries a unit charge, but only half as much, if it carries a double charge. To illustrate: The passage of 96,500 coulombs through a dilute solution of *sodium sulphate* will free one gram ion of *sodium* (or about 23 g.) at the cathode, and one-half of a gram ion of *SO<sub>4</sub>* (or about 48 g.) at the anode. In this case there will be subsequent **reactions at both electrodes** (cf. p. 74), since neither *Na* nor *SO<sub>4</sub>* are stable in the presence of water. These reactions are as follows:



\* The electrical unit of quantity.

According to these equations, we shall have 1 g. of *hydrogen* as a final product in place of 23 g. of *sodium*, and 8 g. of *oxygen* in place of 48 g. of  $SO_4$  (cf. Introduction, page 35 et. seq).

We observe that 1 g. of *hydrogen* is produced when 96,500 coulombs pass through a solution of *sodium sulphate*, or a solution of *hydrochloric acid*. If the electrolysis results in *hydrogen* at all, irrespective of the nature of the solution electrolyzed, liberation of one gram ion will correspond to the passage of 96,500 coulombs. Moreover, this result is not influenced by the temperature of the solution, its concentration, the specific character of the current, etc.

The quantitative relations connecting the passage of electricity through an electrolyte with the decomposition products at the electrodes, which we have pointed out pursuant to primary assumptions of the *Electrolytic Dissociation Theory*, were clearly enunciated by **Faraday** on experimental grounds a half century before this theory was proposed. Obviously, these facts were of fundamental importance in shaping the theory. **Faraday's Law** may be stated as follows:

(a) *The amount of every substance resulting from decomposition by electrolysis, is directly proportional to the quantity of electricity which has passed through the electrolytic conductor.*

(b) *Chemically equivalent amounts of different substances result from all decomposition which is effected by the same quantity of electricity.*

In bringing about chemical decomposition by electrical agency, many specific details, such as current strength, voltage, temperature, form of cell, concentration and nature of conducting mixture, must be suitably regulated to secure efficient results, or indeed, any results at all. But, once the process is operative under any conditions, rigid adherence to the above principles obtains.

Problem: *If the passage of a certain quantity of electricity through a solution of copper sulphate deposits 0.3 g. copper, how much silver will the same quantity of electricity deposit from a solution of silver nitrate?*

One atomic quantity of *copper* is chemically equivalent to two atomic quantities of *silver*, as is apparent on comparison of the

formulas  $\text{CuSO}_4$  and  $\text{AgNO}_3$  with the formulas  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ . That is,  $\text{Cu} \equiv 2\text{H}$ ,  $\text{Ag} \equiv \text{H}$ , and, consequently,  $\text{Cu} \equiv 2\text{Ag}$ .  

$$(63.6) \quad (2 \times 107.9)$$

Applying **Faraday's Law** (b):  $2 \times 107.9$  parts by weight of *silver* will be deposited by the same quantity of electricity which deposits 63.6 parts by weight of *copper*. A simple proportion shows how much *silver* corresponds to 0.3 g. *copper*:

$$63.6 : 215.8 :: 0.3 : x.$$

$$x = 1.02 \text{ (grams of silver deposited).}$$

We have seen that the *Electrolytic Dissociation Theory* consistently accounts for those associated phenomena peculiar to aqueous solutions of electrolytes, which we cited first of all on the opening page of this chapter, namely, their conduction of the galvanic current, abnormal osmotic pressure, etc. The absence of such phenomena in connection with non-aqueous solutions of electrolytes and aqueous solutions of non-electrolytes (cf. general discussion, page 69) is explained by assuming that no electrolytic dissociation takes place in these cases.

The chief value of the theory to the student of Chemistry lies in its power to throw light on the nature of chemical processes which take place between solutions of acids, bases, and salts. We have already observed that such reactions possess significant features (page 69), and we may infer, with all propriety, that the ions resulting from electrolytic dissociation are actively concerned in producing these results.

Before proceeding with a detailed description of chemical action, in this connection, it is essential that we obtain some general idea relative to the actual proportion of acid, base, or salt molecules, which are dissociated when the given substance is dissolved in varying amounts of water. First, we shall consider how such information may be deduced from experimental evidence.

For this purpose, the electrical properties of the solution may be investigated, or determination of the osmotic pressure, freezing-point depression, etc., may be chosen. A brief discussion of the relation between the freezing-point depression in an aqueous solution of *common salt* (containing 1 g. mol.  $\text{NaCl}$  per liter) and the number of dissolved particles, was presented at

the close of Chapter VI, by way of introduction to the *Electrolytic Dissociation Theory*. It seems expedient at this point, to show by enlarging upon the earlier discussion how the proportion of dissociated molecules, or **degree of dissociation** may be calculated from freezing-point measurements in any ordinary case.

At the outset, we assume that the freezing-point depression is proportional to the number of particles of dissolved material, irrespective of their nature, i.e., whether ions or molecules.\*

Suppose half the molecules of a given electrolyte are dissociated in an aqueous solution of a certain concentration, and that

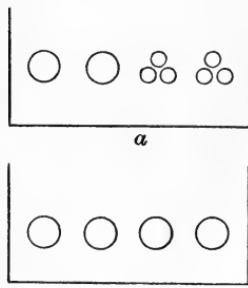


Fig. 6

each dissociating molecule furnishes three ions. Then, if four molecules were originally introduced, eight particles would result,—two whole molecules and six ions. In case no dissociation had taken place, four molecules would be present in the solution. The relation between the freezing-point depression in these two instances would be 8 : 4, following the numerical distribution of particles, as shown graphically in Fig. 6, *a* and *b*.

The number of particles present in the solution (*a*) for every original molecule introduced, could be determined by dividing the actual freezing-point depression measured in this solution, by the normal depression which would correspond to the same quantity of the dissolved substance, if it did not dissociate. Thus,

the depression in (*a*) divided by the depression in (*b*) would equal 2, indicating that there are twice as many particles in (*a*) as molecules originally taken. We should note that the actual depression refers to that obtained by experiment, while the normal depression must be calculated by applying the formula

$$M = \frac{100 Kw}{LW} \quad (\text{cf. Chapter III, pages 53 and 4}), \text{ in which } M, K, w,$$

and *W*, are known. The small letter (*i*) was introduced by van't Hoff (to whom the theory connecting the various proper-

\* According to Raoult's Law, any kind of molecule is equally efficient in lowering the freezing point of a solvent. We attribute the same efficiency to any ion, an assumption which is fully justified by agreement between results resting on this basis, with others furnished by an entirely independent method.

ties of dilute solutions is mainly due) as a coefficient expressing the numerical relation between an actual depression (boiling-point elevation, osmotic pressure, etc.) and the corresponding normal value.

It is thus clear that the determination of ( $i$ ) may be realized experimentally from freezing-point measurements, etc., without previous knowledge of the degree of dissociation.

Now, we may easily obtain an expression for the degree of dissociation, in terms of ( $i$ ) and one other fundamental quantity, known in any specific instance, namely, the number of ions resulting from one dissociating molecule, which enables us to calculate the degree of dissociation at once. For:

Let ( $m$ ) represent the degree of dissociation, and ( $n$ ) the number of ions formed when one molecule dissociates.

Then, from a unit number of molecules originally taken ( $m$ ) are dissociated and ( $1 - m$ ) are undissociated. In place of each molecule which dissociates, there are ( $n$ ) ions, making a total of ( $nm$ ) ions in the solution. Thus, the solution contains ( $1 - m$ ) undissociated molecules and ( $nm$ ) ions, or ( $1 - m + nm$ ) particles, for every unit number of molecules originally taken. Placing this total equal to ( $i$ ) which has the same significance, and solving for ( $m$ ) we obtain:

$$m = \frac{i - 1}{n - 1}.$$

A glance at the diagram (Fig. 6) will serve to fix this relation clearly in mind. In the case represented,  $i = 2$ , as previously noted, and  $n = 3$ . Whence,  $m = 0.50$ , corresponding to our original assumption that half of the molecules were dissociated.

**A far more accurate and convenient method for determining the degree of dissociation is based on (electrical) conductivity measurements.** During our discussion of electrolysis, we observed that electricity is carried through the solution by the ions. The ability of a solution to conduct the current, i.e., to effect an apparent transfer of positive electricity from the anode to the cathode, must depend on the number of ions which carry the electricity (since each carries a fixed amount), and their industry in performing the task. We may define the specific conducting power of any solution by measuring the quantity of

electricity which passes in a unit time between ideal electrodes situated at opposite sides of a unit cube containing the solution at 0° C., when a unit electrical force is applied. If the solution in question is further diluted, a lesser amount of dissolved substance is included in the unit volume than before. Consequently, the electricity which would be carried from one electrode to the other by all the ions resulting from the amount of substance previously contained in one cubic centimeter, is equal to the sum of that carried by the ions in every unit volume of the diluted solution. In other words, the total conductivity due to all the ions, is equal to the *specific conductivity* multiplied by the number of cubic centimeters in which the given amount of substance is dissolved. We commonly refer such measurements to one gram molecule of dissolved substance, and use the term, *molecular conductivity*, to define the product of specific conductivity into the number of cubic centimeters of solution containing one gram molecule.

Now, the rate at which the ions move\* under the influence of a given electrical force is known to be practically independent of the concentration, in the case of dilute solutions. Therefore, the respective quantities of electricity which will pass through two unequally concentrated solutions of the same electrolyte at the same temperature† in a definite time interval under the influence of the same electrical force, will be proportional to the other conductivity factor, i.e., the numbers of ions which carry the electricity in each respective solution. Thus, we see that separate determinations of the molecular conductivity at a number of different concentrations serve to show the relative extent to which the dissolved substance is dissociated when dissolved in these different amounts of water — or, what amounts to the same thing, the relative numbers of dissociation products, i.e., ions.

\* Substances giving colored ions are used in demonstrating the movement of ions visually. Their rate of motion is uniformly slow, but varies considerably with the nature of the ion. Velocities of only a few centimeters per hour are commonly associated with the ordinary ions, even when driven by very considerable electrical forces. The solvent medium evidently offers enormous resistance to the motion of these extremely minute particles.

† Temperature elevation causes an increase in conductivity by reason of the resulting increase in the velocity of the ions.

To pass from this relative information, to an actual knowledge of the *degree of dissociation* at any dilution, it is necessary that the molecular conductivity corresponding to complete dissociation be ascertained. It has been found that the molecular conductivity invariably increases with the dilution up to a certain point, which may be called infinite dilution, when it remains constant, notwithstanding further dilution. Evidently, the maximum of conductivity has then been attained, owing to the presence of the greatest possible number of ions. We are, therefore, at liberty to assume that the dissolved substance is completely dissociated.

*To obtain the degree of dissociation at any lesser dilution, we divide the molecular conductivity, at this dilution, by the molecular conductivity at infinite dilution.* The logic of this process is indicated below:

$$\frac{\text{Mol. Cond. at dilution A}}{\text{Mol. Cond. at infinite dilution}} = \frac{\text{No. of ions at dilution A}}{\text{Greatest poss. no. ions}}$$

$$= \frac{\text{No. of diss'd mols. at dilution A}}{\text{Total no. of mols.}}$$

$$= \text{Degree of Dissociation at dilution A.}$$

Conductivity data (taken from Kohlrausch's tables), referring to aqueous solutions of *sodium chloride* at 18° C., follow:

Volume in Liters Containing One Gram Mol. NaCl.	Molecular Conduc- tivity.	Degree of Dissoci- ation.
1	74.35	$\frac{74.35}{108.99} = 0.681$
5	87.73	$\frac{87.73}{108.99} = 0.805$
10	92.02	$\frac{92.02}{108.99} = 0.844$
100	101.95	$\frac{101.95}{108.99} = 0.935$
1000	106.49	$\frac{106.49}{108.99} = 0.977$
5000	107.82	$\frac{107.82}{108.99} = 0.989$
10,000	108.10	
Infinite volume	108.99 (calculated)	Dissociation com- plete.

It is apparent from these conductivity data that one gram molecule of sodium chloride is completely dissociated into ions when dissolved in 10,000 liters or more of water. Moreover, we see that any ordinary aqueous solution of *sodium chloride* such as might be used in the laboratory, contains a larger percentage of dissociated, than undissociated molecules.

Much experimental work has been undertaken to determine whether these different methods for obtaining the *degree of dissociation* give concordant results, as should be the case if our theory is reliable. Satisfactory agreement between corresponding results has always attended such comparative study. The superiority of the conductivity method over the freezing point, boiling point, vapor pressure, or osmotic pressure methods, both in point of facility in experimentation and accuracy of results, is responsible for its general adoption in pursuing the study of electrolytic dissociation phenomena.

We may now proceed to inquire into the characteristic dissociation features of the three different chemical varieties of electrolytes, namely, acids, bases, and salts. The *degree of dissociation* of each invariably increases with the dilution — water as the dissociating agent, operates more effectively as its own concentration increases. However, equal molecular quantities of different substances are by no means dissociated to the same extent when dissolved in the same quantity of water. Differences in this respect serve as the basis for a detailed theoretical explanation of chemical interaction between aqueous solutions of electrolytes. The very general outline of the comparative dissociation of different electrolytes, given in the next three paragraphs, will enable us to draw some important conclusions regarding their tendency to interaction.

A wide range of variation is observed on comparing the *degree of dissociation* for different acids in solutions of the same molecular concentration. The comparative dissociation of some common acids when dissolved in water to the extent of one-tenth gram molecule per liter is shown by the following very approximate percentage numbers:  $\text{HNO}_3$ ,  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI}$  .... 90 (90 per cent of all the dissolved molecules are dissociated);  $\text{H}_2\text{SO}_4$  .... 60;  $\text{H.C}_2\text{H}_3\text{O}_2$  .... 1.5;  $\text{H}_2\text{CO}_3$  .... less than 0.2;  $\text{H}_2\text{S}$  .... less than 0.1;  $\text{H}_3\text{BO}_3$  .... 0.01. Whatever the acid, its aqueous

**solution must contain hydrogen ions.** We attribute such properties as are common to all aqueous acid solutions, i.e., their sour or "acid" taste, action on litmus, and other general chemical reactions, to these *hydrogen ions*. In proportion as the solution contains *hydrogen ions*, these properties will be more marked. Thus, it is logical to say that the strength of the acid depends upon the concentration of *hydrogen ions* in its solution. From a comparative standpoint, *hydrochloric acid* is stronger than *sulphuric acid*, because it furnishes a greater concentration of *hydrogen ions* when dissolved in water; *acetic acid* is weak, while *boric acid* is extremely weak.

Similar diversity characterizes the dissociation of bases. **The aqueous solution of a base must contain hydroxyl ions.** The common strong bases (those yielding *hydroxyl ions* in quantity when dissolved in water) with their approximate dissociation values, expressed as for acids in the preceding paragraph, are:  $\text{NaOH}$ ,  $\text{KOH}$  .... 90;  $\text{Ba}(\text{OH})_2$  .... 75; and  $\text{Ca}(\text{OH})_2$  .... very highly dissociated in a solution containing about one-fiftieth of a gram molecule per liter, which solution represents about the limit of its solubility at ordinary temperature. A large number of weak bases are known, most of them rather insoluble in water. Of these, one is very soluble, and quite indispensable as a laboratory reagent —  $\text{NH}_4\text{OH}$  .... 1.5. Others are:  $\text{Cu}(\text{OH})_2$ ,  $\text{Cd}(\text{OH})_2$ ,  $\text{Zn}(\text{OH})_2^*$ ,  $\text{Mn}(\text{OH})_2$ ,  $\text{Fe}(\text{OH})_2$ ,  $\text{Co}(\text{OH})_2$ ,  $\text{Ni}(\text{OH})_2$ ,  $\text{Pb}(\text{OH})_2^*$ ,  $\text{Sn}(\text{OH})_2^*$ ,  $\text{Bi}(\text{OH})_3$ ,  $\text{Sb}(\text{OH})_3$ ,  $\text{Fe}(\text{OH})_3$ ,  $\text{Al}(\text{OH})_3^*$ ,  $\text{Cr}(\text{OH})_3$ , — all insoluble, and weakly basic; the last four considerably weaker than those preceding.

\* These very sparingly soluble substances, although commonly regarded as bases, give hydrogen ions, as well as hydroxyl ions, both in minute concentrations. Thus, they possess weakly basic and acidic properties in common and are called *amphoteric electrolytes*. From the acid standpoint, we may write their formulas:  $\text{H}_2\text{ZnO}_2$ ,  $\text{H}_2\text{PbO}_2$ ,  $\text{H}_2\text{SnO}_2$  and  $\text{H}_3\text{AlO}_3$ , and those of their sodium salts, which are all soluble (i.e., the acids dissolve in sodium hydroxide):  $\text{Na}_2\text{ZnO}_2$  (sodium zincate),  $\text{Na}_2\text{PbO}_2$  (sodium plumbite),  $\text{Na}_2\text{SnO}_2$  (sodium stannite) and  $\text{Na}_3\text{AlO}_3$  (sodium aluminate);  $\text{NaAlO}_2$ , derived from  $\text{H}_3\text{AlO}_3 - \text{H}_2\text{O}$ , or  $\text{HAIO}_2$ , is also known. Chromium hydroxide also dissolves in (cold) sodium hydroxide, giving a salt of the formula,  $\text{NaCrO}_2$ .

In nearly every instance, neutral salts are dissociated to an extent approximating that of strong acids or bases. While a somewhat narrower classification of dissociation values according to the formula types of salts may be offered, it is of greatest importance to note that seldom less than 50 per cent of a salt is dissociated in an aqueous solution containing 0.1 gram molecule per liter. Since some salts are very insoluble, and many relatively so, it is clear that we are not always able to obtain a highly concentrated solution of ions by placing a large quantity of salt in a small volume of water. *Neither the positive hydrogen ions, which characterize acid solutions, nor the negative hydroxyl ions, which characterize basic solutions, can be present in neutral salt solutions.*

Pure water is dissociated to a very slight extent. Calculations based on conductivity results, have shown that it takes several hundred million gram molecules of water to furnish one gram ion of *hydrogen* and one gram ion of *hydroxyl* — its dissociation products.

The process which we have called **electrolytic dissociation** or **ionization** stops (in common with other dissociation phenomena) when all the changing material has reached a final state of adjustment, according to the dictum of certain ruling conditions. We made use of the term *equilibrium* in the introductory chapter (page 30), to describe this general condition, and alluded to the conventional use of reversed arrows in an equation to indicate the simultaneous presence of all the reacting constituents and the possibility of displacing the equilibrium in either direction.

The significance of the following expression for the electrolytic dissociation of *hydrochloric acid* should, then, be clear:



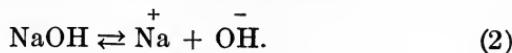
We have seen that the relative amounts of these different substances are primarily dependent on the dilution; that, the greater the dilution, the more ions produced; and that, for any given dilution, the actual amounts of all three are defined.

Experience teaches us, furthermore, that *this condition of equilibrium is instantly established when the material is dissolved in water.*

Bearing these facts in mind and recalling what has been said on the previous page about the relative dissociation of different

electrolytes, let us proceed to consider the effect of mixing certain of them in aqueous solution.

Suppose one-tenth of a gram molecule of *hydrochloric acid* is dissolved in a half liter of water and mixed with a solution prepared by dissolving one-tenth of a gram molecule of *sodium hydroxide* in a half liter of water. We now have one-tenth of a gram molecule each of *hydrochloric acid* and *sodium hydroxide* in a liter of water unless some chemical reaction has taken place. Equation (1) — above — shows the three substances present in an aqueous solution of *hydrochloric acid*; equation (2) — below — supplies similar information relative to the solution of *sodium hydroxide*; while we are told on pages 82 and 83 that both (strong) acid and (strong) base are some 90 per cent dissociated in an aqueous solution of this concentration.



In the light of our present information, should any change have occurred on mixing these two solutions? Most assuredly, since two other pairs of ions ( $\overset{+}{\text{Na}} + \overset{-}{\text{Cl}}$ ) and ( $\overset{+}{\text{H}} + \overset{-}{\text{OH}}$ ) must attain a proper state of adjustment with the undissociated molecules corresponding to their union, i.e., the molecules which would form them, by electrolytic dissociation, on being brought into an aqueous medium.

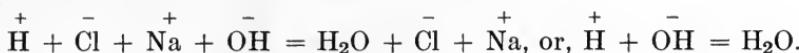
Therefore, we write the additional equations (3) and (4):



Now, a dilute solution of *sodium chloride* consists mainly of ions. One-tenth of a gram molecule of *sodium chloride* in one liter of water is about 84 per cent dissociated (cf., page 81); hence, there can be no extensive combination of *sodium ions* with *chloride ions* in this solution. — Reaction (3) will proceed only to a certain slight extent in the right-hand direction.

On the other hand, *water* is scarcely dissociated at all, and we must expect an almost complete disappearance of *hydrogen* and *hydroxyl ions*, resulting in the production of *undissociated water*. — Reaction (4) will proceed liberally in the right-hand direction. This extensive removal of *hydrogen* and *hydroxyl ions* has

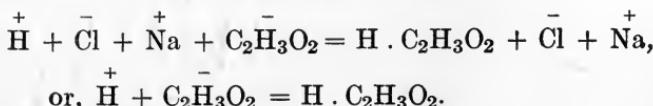
destroyed the balance between *undissociated acid* and its ions (1), as well as that between *undissociated base* and its ions (2). Consequently, some of the ten per cent — more or less — of *undissociated acid*, which was in the solution, will dissociate until readjustment is secured, and the *undissociated base* will behave in the same way. *Hydrogen* and *hydroxyl ions* from this secondary dissociation will combine, as before, to form *water*, necessitating further dissociation of acid and base. Progressive action of this sort ensues, until practically all of the *hydrogen* and *hydroxyl* primarily contained in the acid and base, respectively, have been transformed into *undissociated water*. Thus, we may use the following equation to express the essential change, neglecting the undissociated acid and base:



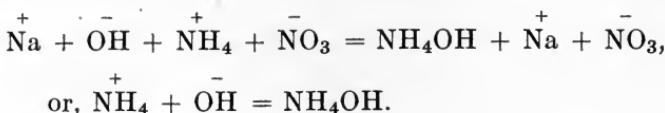
If the solution is evaporated, the *sodium* and *chloride ions* unite to form *undissociated sodium chloride*.

The student has, without doubt, recognized the above process as that of **neutralization**. It should be quite clear that whatever the acid or base used in neutralizing one another, provided both are strong — largely dissociated — the essential feature of the process is identical, i.e., *the formation of water*. This theoretical conclusion is substantiated by the fact that, in separate cases of neutralization, the thermal change during the reaction is always the same, if equivalent amounts of acid are used (to guarantee the production of identical amounts of water in all cases).

No difficulty will be met in adapting the above reasoning to **other reactions**, in which ions from highly dissociated substances, by their combination, may form much less dissociated substances. Such reactions are generally less complete than the neutralization process, since the products are much more dissociated than water. Thus, a solution of any common strong acid, such as *hydrochloric acid* will interact with a solution of *sodium acetate* (or any salt of a weak acid) to form a certain amount of *acetic acid* (or the corresponding acid). The essential feature of such a reaction is the union of ions, as follows:



In the same way, a strong base may be used to free a weaker base from its salts:



Of particular interest, is the **reaction between solutions of two different salts**. We note, here, that there is no great difference in the *degree of dissociation*, pertaining to different salts, but that there may be great difference in the *solubilities of the salts*.

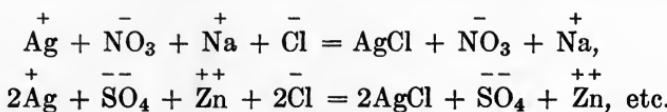
Consider the salt *silver chloride* which is very insoluble in water. When in contact with water, a certain (very limited) amount dissolves. At any given temperature, the solution must contain a perfectly definite amount, if it is kept in contact with the solid, i.e., if the solution is saturated at the given temperature. Now, another definite relation must exist between the molecules of dissolved *silver chloride* and the ions which it has formed immediately on attaining the dissolved condition. There is, then, a final state of adjustment requiring the presence in the solution of a fixed amount of undissociated  $\text{AgCl}$  maintaining a fixed concentration of  $\text{Ag}^+$  and  $\text{Cl}^-$  ions.

Suppose, in some way, enough *silver* and *chloride* ions were brought into a liter of water to represent one-tenth of a gram molecule of *silver chloride*. Then, if the salt dissociated to about the same extent as *sodium chloride*, some ten per cent of this total quantity of *ions* would unite to form undissociated  $\text{AgCl}$ , which would have to remain in solution to keep the remaining ions inactive. This would, however, be an amount most overwhelmingly in excess of that which can actually dissolve; hence, it would almost completely **precipitate**, and the ions would continue to furnish undissociated material, likewise precipitating, until their concentrations became reduced to the values normally consistent with the final concentration of dissolved *silver chloride* molecules.

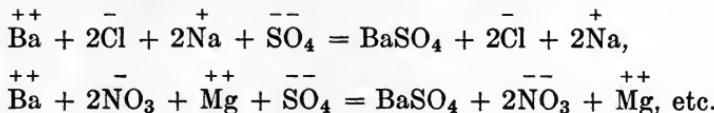
Now, whenever solutions of a *soluble silver salt* and a *soluble chloride* are mixed, the general condition just considered is realized. That is, appreciable concentrations of *silver ions* and *chloride ions* are brought within range of one another. Precipitation of *silver chloride* will therefore result until practically all

the *silver* and *chlorine* in the initial substances is deposited in this form.

Such characteristic formation of insoluble products is of service in identifying the materials which participate in the change. We must, however, fully appreciate the limitations of any one **precipitation test**, — it reveals the identity of only part of each reacting substance — in the above case, *silver* from the dissolved silver salt and *chlorine* from the dissolved chloride. It is, therefore, most consistent to refer the whole process to the *Electrolytic Dissociation Theory* by defining each test in terms of its critical factors, the *ions*. Thus, the **silver ion** is a test for the **chloride ion**:



And, the **barium ion** is a test for the **sulphate ion**:



If we mix solutions of two soluble salts, the ions of which by altered recombination form two other soluble salts, there will, of course, be no precipitation. On continued evaporation of the solution, that salt, of the four, which first reaches saturation, will be the first to deposit. There is, in general, no appreciable thermal change on mixing different dilute salt solutions, since no extensive formation of undissociated molecules results. A solution containing one-fifth of a gram molecule of *sodium nitrate* per liter when mixed with an equal volume of a solution containing one-fifth of a gram molecule of *potassium chloride* per liter, contains the same material, disposed in the same manner, as a mixture made from one-fifth of a gram molecule of *sodium chloride* and one-fifth of a gram molecule of *potassium nitrate* in the same volume. All four salts will be present to about the same slight extent in the undissociated condition, and about 80 per cent of the total material will be in the form of ions.

An adequate perception of the varied possibilities of chemical change due to "crosswise" combination between two pairs of

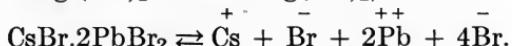
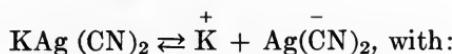
ions, should follow a careful reading of the last few pages. The quantitative aspect of such change will be made the subject for some additional discussion at the close of the chapter on Mass Action. Before proceeding to this special subject, however, some further remarks relative to the general bearing of ion formation on chemical change, will be introduced:

No great amount of experience in the chemical laboratory is required to teach us that the precipitated compounds of certain metals are more or less soluble in ammonia. To the beginner, silver and copper are most prominent in this connection. While a detailed consideration of the solution process in such cases is beyond the scope of this text, it may be stated, in general terms, that the addition of ammonia to such a body, results in the formation of a soluble compound yielding **complex cations** containing ammonia, in place of the *simple metal cations*. Thus, silver chloride dissolves in ammonia, and the resulting solution contains,  $\text{Ag}^+ \cdot 2\text{NH}_3^-$  ions and  $\text{Cl}^-$  ions — the original  $\text{Ag}^+$  ions have combined with  $\text{NH}_3^-$  to form complex *silver-ammonia particles*, each carrying the single positive charge originally carried by the silver alone. The complex *copper-ammonia cation*,  $\text{Cu}^+ \cdot 4\text{NH}_3^-$ , is deep blue in color, hence the use of ammonia in testing for the presence of copper.

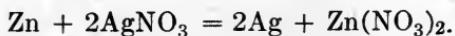
The solvent effect of solutions of the alkali cyanides ( $\text{KCN}$ , or  $\text{NaCN}$ ) on many metallic compounds, is likewise due to the formation of complex ions. In such cases we have **complex anions** instead of complex cations. Thus, silver cyanide is soluble in a solution of *potassium cyanide*, the  $\text{CN}^-$  ions having united with  $\text{AgCN}$  to form  $\text{Ag}^+ \cdot (\text{CN})_2^-$  ions, which, with  $\text{K}^+$  ions, constitute the dissociation products of the soluble salt,  $\text{KAg}(\text{CN})_2$ . The individuality of any complex ion is reflected in its chemical behavior. Its reactions are quite different from those of the ion or ions from which it was generated. For example, solutions containing the *complex silver-ammonia ion*, mentioned above, do not precipitate silver chloride on the addition of chloride ions, i.e., an ammoniacal solution of silver nitrate fails to precipitate silver chloride when mixed with a solution of sodium chloride. Usually, however, such an ion is very unstable, tending to pass

into the simpler state, unless conditions most favorable to its non-alteration are maintained. Invariably, the solution containing any complex ion also contains a very inconsiderable complement of simple ions, which have resulted from its dissociation. Hence, the introduction of another ion, which may give a sufficiently undissociated — in effect, sufficiently insoluble — compound with the simple ion to actually reduce its normal concentration in the solution, will cause the complex ion to supply this deficiency — which becomes progressive — by breaking up, and we shall have, as a final result, the characteristic reaction of the simple ion. Thus, *hydrogen sulphide* precipitates the *copper* from an *ammoniacal solution of any copper salt*, which must contain  $\text{Cu} \cdot 4\text{NH}_3$  ions, to the almost complete exclusion of  $\text{Cu}$  ions, just as it would from *an acid solution* (which could contain only  $\text{Cu}^{++}$  ions), because the compound *copper sulphide* ( $\text{Cu}^{++} \text{S}^{-} = \text{CuS}$ ) is extremely insoluble, maintaining a lesser concentration of  $\text{Cu}$  ions than does the complex ion itself.

There is a wide difference between a salt which gives a **complex ion** when dissolved in water, and a **double salt** (cf. Introduction, page 26). The latter dissolves in water to give the simple ions of its constituent salts. By way of illustration, contrast:



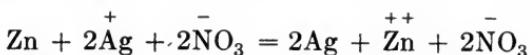
We have made early note of that general type of reaction in which one elementary kind of matter drives another kind out of its state of combination with another or other elements, usurping its place (cf. Introduction, page 31). Reactions of this sort, or **replacements**, as we have named them, may be very easily brought into harmony with the general scheme of ionic disposition and transfer of material, which we have been considering. Let us first turn to the replacement of one positive element by another in a reaction such as the following:



Study of many reactions like the above has led to an empirical arrangement of the positive elements, i.e., the metals and hydrogen, in an order representing their successive ability to replace one another. Each metal in the accompanying list will replace those metals which follow. The metals preceding hydrogen will replace it in an acid — they dissolve in acid with evolution of hydrogen.\*

Mg	Zn	Fe	Sn	Pb	H	Cu	Hg	Ag	Au
----	----	----	----	----	---	----	----	----	----

Writing the reaction between *zinc* and *silver nitrate* in the ionic form:



it appears that the *zinc*, which had no charge at the outset, has assumed the charges previously held by two *silver ions*, releasing these atoms of *silver* from the ionic condition. Evidently the *zinc* has a greater tendency to enter this condition than *silver*. To describe this general tendency of metals to enter solution, implying, of course, the formation of ions,† we use the words, **electrolytic solution tension**. The metals are arranged in the above list, according to their decreasing electrolytic solution tension.

A better understanding of the replacement process is obtained by picturing the sequence of changes which would logically follow a difference in **electrolytic solution tension between the two metals**.

Suppose a *zinc* strip to be suspended in a vessel of pure water. The expansive force tending to send *zinc ions* out into the liquid immediately becomes operative. Every *zinc ion* carries two unit positive charges of electricity, and since the zinc particle has assumed this positive electrification on leaving the strip, the latter must have assumed an equivalent negative electrification. When a number of ions have been projected into the liquid, they

\* Lead fails to dissolve in the ordinary dilute acids, owing to the insolubility of its salts — as soon as an appreciable amount of salt is formed, this acts as a protective coating to prevent further action.

† The metals dissolve only in the ionic condition.

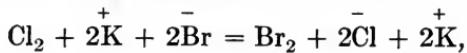
will forcibly repel one another, owing to their like charges and the absence of partners carrying opposite charges. Consequently, they will be continually projected within the immediate sphere of attraction of the strip and will tend to reattach themselves to it. On the other hand, it becomes increasingly difficult, as ions enter the liquid, for others to leave the strip in the face of its constantly accumulating negative charge. The magnitude of this electrostatic force opposing the accumulation of ions in the solution is very great, even when only a few ions are concerned, since each ion carries a very considerable charge. We therefore assume that, before a measurable quantity of ions has entered the solution, successful opposition to the electrolytic solution tension of the metal has been set up, so that a condition of balance is maintained.

Although the electrolytic solution tension of *zinc* causes a number of *zinc ions* to remain in solution in the face of this opposing force, ions from a metal of lesser electrolytic solution tension would be driven by its agency to the zinc strip. Action of this sort ensues when the strip is immersed in a solution of *silver nitrate*. When two *silver ions* reach the strip, two of its negative charges are used in neutralizing their two positive charges. The solution has now lost two positive charges and the strip has lost two negative charges; hence, the electrical force operating against the electrolytic solution tension of *zinc*, is reduced sufficiently to permit one more *zinc ion* to enter the solution, whereby this force is restored to its former value. Thus, we see that two atoms of *silver* have been deposited, one atom of *zinc* has entered the solution as an ion, and the system is again in position to repeat the process.

Closely related to the electrolytic solution tension of a metal is the electrical pressure (electromotive force) required to drive the metal out of solution (during electrolysis). As would be expected, the order which the metals assume, according to their decreasing electrolytic solution tension, is preserved when the respective values for the electromotive force necessary to decompose equally concentrated (in molecular quantities) solutions of their salts are made the basis for gradated arrangement.

The **negative elements** are equally characterized by a specific tendency to enter the ionic condition. Here, we are dealing with

soluble substances, for the most part. One of the familiar halogen replacements is represented by the following reaction:



which may be interpreted in the same general way as the Zn-Ag replacement.

## CHAPTER VIII.

### THE LAW OF CHEMICAL MASS ACTION.

The reversible nature of chemical action has been pointed out and emphasized in earlier portions of this book. The phenomena of electrolytic dissociation, considered in the last chapter, offer abundant illustration of this principle. Reactions in general between substances, however disposed, whether gaseous, liquid, solid, ionic, etc., proceed more or less completely in either direction, in measure determined by the prevailing physical conditions, i.e., temperature, pressure, concentration, nature of solvent, etc.

The electrolytic dissociation of an acid, base, or salt in aqueous solution is very little influenced by the temperature or pressure, but varies from 0 to infinity with the concentration. Many gaseous substances dissociate into simpler gaseous substances. The extent of such dissociation is primarily dependent on the temperature and pressure. In any specific case, concentrations of the initial substance and its dissociation products will be perfectly defined for any given temperature and pressure. If the temperature is raised (at constant pressure), more gas dissociates; if lowered, some of its dissociation products recombine.

In the laboratory, we are accustomed to work under rather constant conditions of temperature and pressure. To be sure, reaction mixtures are heated, cooled, enclosed in sealed tubes so that the pressure may rise, or placed in connection with a vacuum pump, to bring about desired results, but withal, certain approximately defined temperatures and pressures — such as, "room temperature," "low redness," "ordinary pressure," "diminished pressure," etc. — are commonly maintained, and it is the concentration factor which is subjected to wide variation.

The term, **dissociation** implies reversibility, or a reciprocal tendency of the dissociation products to reunite. While other processes, involving more than one initial substance are equally

important as examples of reversible reaction, attention is first drawn to this particular class of phenomena on account of its simplicity.

The case of gaseous dissociation represented by the equation:



is frequently chosen to illustrate the subject in hand, since both changes may be brought about with ease and a marked difference in color between the two varieties of molecules renders the general state of the mixture apparent at a glance.

Undissociated nitrogen tetroxide molecules ( $\text{N}_2\text{O}_4$ ) are colorless, while the simpler molecules ( $\text{NO}_2$ ) are reddish brown. Under ordinary conditions, the gas is distinctly colored, consisting of both  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  molecules. Each variety constitutes a certain definite proportion of the mixture. If more  $\text{NO}_2$  molecules could be added and the temperature and pressure kept constant, the color of the mixture would not deepen, but the reaction would proceed towards the left until a sufficient number of  $\text{N}_2\text{O}_4$  molecules had been formed to restore the proportion of each variety to its original value. At a lower temperature the mixture contains fewer  $\text{NO}_2$  molecules. This may be shown by immersing a sealed tube containing the gas in a vessel of ice water, when the color practically disappears. On gently warming the tube, the color returns and becomes more pronounced as  $\text{NO}_2$  molecules continue to be formed — as the reaction proceeds towards the right.

Gaseous *hydriodic acid* dissociates into *hydrogen* and *iodine* at temperatures above some  $200^\circ$ :



If the acid is enclosed in a sealed tube at room temperature and atmospheric pressure and then heated to about  $500^\circ$ , approximately 20 per cent will be dissociated. A mixture of *hydriodic acid*, *hydrogen*, and *iodine* in any proportions whatever, if brought under the same condition of temperature and pressure as in the above case, will readjust itself — by reaction towards the right or left as needs be — to attain a final composition identical with the above.

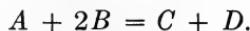
At some higher temperature, approximating  $800^{\circ}$ , the diatomic *iodine* molecules begin to dissociate:



This dissociation becomes complete at about  $1500^{\circ}$ .

We conceive that the two reactions corresponding to any reversible change take place simultaneously. When both progress at an equal rate, the actual amounts of all the reacting substances remain unaltered, i.e., a condition of equilibrium results. A brief outline of the imaginative working of such a process from the standpoint of the kinetic theory, will serve to bring about a better understanding of these relations.

For this purpose, we will consider the substances *A* and *B* enclosed in a suitable receptacle and elevated to a temperature at which reaction occurs, with formation of the new substances *C* and *D*, according to the equation:



We may reason that the impacts of the rapidly moving *A* and *B* molecules are responsible for their chemical alteration — breaking apart and reuniting in the form *C* + *D*. One molecule of *A* must meet two molecules of *B* to determine change as prescribed by the above equation. But it is not necessary to assume that every impact of this sort results in chemical change. The *A* and *B* molecules move with a certain average velocity dependent on the temperature. Of two individual molecules chosen at random, however, one may move faster than the other. Consequently, some of the *A*-*2B* impacts will be more forcible than others, or more likely to cause alteration. The number of impacts which are effective in this respect must, in any event, be proportional to the total number of impacts. In other words, the rate at which the substances *A* and *B* combine to form the substances *C* and *D* is proportional to the rate at which one *A* molecule meets two *B* molecules.

In the same manner, we reason that the rate at which the substances *C* and *D* combine to form the substances *A* and *B* is proportional to the rate at which one *C* molecule meets one *D* molecule.

For a time, the rate at which *A* and *B* combine will be greater than the rate at which *C* and *D* combine, since the *A* and *B* molecules are in position to impact frequently, being relatively numerous and closely packed at the start, while the *C* and *D* molecules are absent in the original mixture and collide infrequently following their initial appearance. As the reaction proceeds towards the right, *A* and *B* molecules disappear, their collisions become less frequent and the rate of reaction diminishes. On the other hand, as the molecules of *C* and *D* increase in number, their collisions become more frequent and the rate of reaction towards the left increases. Obviously, there will come a time when the rates of both reactions will be equal. Then, as much *A* and *B* as *C* and *D* will be produced in a unit time and the quantities of all four substances will remain unchanged.

Let us consider the **relation between the concentration of each variety of molecules and the rate of reaction** in greater detail. (We ordinarily express the molecular concentrations of different substances in gram molecules per liter. Such concentration values are proportional to the actual numbers of molecules involved.)

The number of impacts between a single chosen molecule of the substance *A* and any of the *B* molecules in a time unit is evidently proportional to the concentration of the latter. During this time, the number of impacts between a single *B* molecule and others of its kind is also proportional to their concentration. But every other *B* molecule has the same opportunity to collide with its fellows, and this aggregate of *B* molecules is represented by — proportional to — the number which expresses their molecular concentration. Therefore, the total number of individual impacts between *B* molecules in a unit time is proportional to the square of their concentration (concentration of *B*  $\times$  concentration of *B*). Now, we have seen that the rate of the reaction towards the right is proportional to the number of *A*-*2B* impacts. Since the number of *2B* impacts is proportional to the square of the concentration of *B* molecules, the number of times one chosen *A* molecule will meet two *B* molecules at once is proportional to the same value; or, the total number of *A*-*2B* impacts due to the motion of all *A* and *B* molecules and consequently, the rate of reaction towards the right, is proportional to the concentration

of *A* molecules, multiplied by the square of the concentration of *B* molecules.

Applying the same reasoning to the reaction towards the left, we conclude that the rate of this reaction is proportional to the concentration of *C* molecules multiplied by the concentration of *D* molecules.

In general, the rate of any reaction is proportional to the concentration of each reacting substance multiplied by itself as many times as its coefficient in the equation for the reaction indicates.

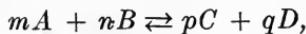
The simple **Law of Chemical Mass Action** announced by **Guldberg and Wange** (Christiania) in 1867, will now appear in a satisfactory light. It may be stated in the following words:

*The rate of chemical action is proportional to the active mass of each reacting substance.*

From the preceding discussion, it is clear that the **mass** of any substance concerned in a reaction where all the material is evenly and equally distributed, is **active** (or efficient in promoting the reaction) *in direct proportion to the number of molecular units in a given volume, which it represents, if only one molecule of the particular substance enters into the equation.* Otherwise, the coefficient representing the number of molecules of the substance required by the equation, must be used as an exponent in connection with this molecular measure, or concentration, to correctly define the relation of the mass of the substance to the change.

This law is of particular service in showing the quantitative relations between different substances in equilibrium with one another, as the result of reversible change.

Suppose the four substances *A*, *B*, *C*, and *D* are concerned in such change, according to the reaction:



where the letters *m*, *n*, *p*, and *q* represent ordinary numerical coefficients. Let the small letters *a*, *b*, *c*, and *d* denote the respective concentrations of each substance; — the term, concentration, is used throughout this chapter in the sense of molecular concentration.

Then the rate of the reaction:

$$mA + nB = pC + qD, \quad (1)$$

is proportional to  $a^m$  and to  $b^n$ , according to the above law. Or, it is equal to a constant quantity multiplied by  $a^m$  and  $b^n$ . Denoting this rate, or velocity, by  $V_1$  and the constant by  $K_1$  we have:

$$V_1 = K_1 a^m b^n.$$

From the transformed equation  $K_1 = \frac{V_1}{a^m b^n}$  we see that  $K_1$  defines the rate of the reaction when the concentration of each reacting substance is 1. That is, when both  $a$  and  $b$  possess the value 1, another rate, just equal to  $K_1$ , will replace  $V_1$ . As the reaction proceeds, the concentrations  $a$  and  $b$  diminish, but the Mass Action Law continues to hold, and the constant  $K_1$  preserves its former significance. To illustrate: At the end of a finite time ( $t$ ) let us assume that the concentration of  $A$  has diminished by an amount ( $m$ ) ( $x$ ) - gram molecules per liter. Then the concentration of  $B$  will have diminished by an amount ( $n$ ) ( $x$ ), since, according to the equation, every time ( $m$ ) molecules of  $A$  react, ( $n$ ) molecules of  $B$  are concerned in the change; and their respective concentrations will have become  $(a - mx)^m$  and  $(b - nx)^n$ . The rate of the reaction will now be equal to  $K_1 (a - mx)^m (b - nx)^n$ , where  $K_1$  denotes, as before, the rate corresponding to unit concentrations of  $A$  and  $B$ .

By strictly analogous reasoning, we place the rate of the reaction:

$$pC + qD = mA + nB, \quad (2)$$

which may be indicated by  $V_2$  equal to a characteristic constant  $K_2$  multiplied by the active masses of the substances  $C$  and  $D$ . Thus:

$$V_2 = K_2 c^p d^q.$$

For the special case of *equilibrium*, the rates of both reactions are equal, and we write:

$$V_1 = V_2, \text{ or } K_1 a^m b^n = K_2 c^p d^q.$$

Whence,

$$\frac{K_1}{K_2} = \frac{c^p d^q}{a^m b^n},$$

which becomes,

$$K = \frac{c^p d^q}{a^m b^n},$$

on substituting a new constant  $K$  for the quotient  $\frac{K_1}{K_2}$ .

We have seen, in the note above, that the constant  $K_1$  represents the rate of reaction (1) when unit concentrations of the substances  $A$  and  $B$  are allowed to react. Hence, it is called the **velocity coefficient** of this reaction. The second constant  $K_2$  is, then, the velocity coefficient of reaction (2).

The ratio of both velocity coefficients  $\frac{K_1}{K_2}$ , or  $K$  bears the name, **equilibrium coefficient**. Its physical significance is as follows:

*When the several substances participating in reversible chemical change have reached a state of equilibrium (whereby no further alteration in their respective concentrations occurs) the product of the active masses of all the substances constituting one set of changing material, divided by the product of the active masses of all the substances constituting the other set of changing material, is equal to a quantity, called the equilibrium coefficient, which possesses the same value for this particular process, at a given temperature, whatever the actual amounts of any or all the substances used at the start.*

In the laboratory, new substances are frequently evolved in the gaseous state by heating a mixture of two salts, a salt and an acid, or a salt and a base. These compounds are always capable of double decomposition or crosswise recombination among themselves, and to determine whether a given pair will proceed to produce the complementary pair on being heated in an open vessel, or will themselves constitute the end products of reaction between the four under these conditions, we have only to apply the principle of mass action, in connection with our general information relative to the physical properties of each substance.

By way of general illustration, let us suppose that the substances  $AB$  and  $CD$  are mixed and heated at first in a closed space. Then we may write the following reversible reaction, indicating that all four compounds  $AB$ ,  $CD$ ,  $AD$ , and  $BC$  are present in certain fixed proportions at any given temperature:



For the sake of simplicity, it is assumed that only one molecule of each substance enters into the equation.

If we denote the equilibrium concentrations of these four sub-

stances by  $C_{AB}$ ,  $C_{CD}$ ,  $C_{AD}$ , and  $C_{BC}$  the state of the mixture is defined by the expression,

$$\frac{C_{AD} \times C_{BC}}{C_{AB} \times C_{CD}} = K,$$

where  $K$  is the equilibrium coefficient.

We should note, however, that this implies an even distribution of all the substances in some form so that no boundary separates one from another. In practice, reaction mixtures are most often heterogeneous, consisting of gaseous, liquid, or solid material without reservation. The reaction may then take place in the liquid phase, as well as in the gaseous phase, and separate equilibrium constants, defined as above, will apply to each. There is, however, a definite numerical relation between these two constants, since the concentration of any gas as dissolved in a liquid, is proportional to the pressure, or concentration, of the gas itself (cf. Introduction, page 20). If a liquid constituting one of the reacting substances plays the part of solvent for the other substances, its active mass as regards this reaction within its own substance is considered constant — its own concentration is bound to be infinitely great in proportion to the concentrations of dissolved material. When solid material participates in equilibrium, its active mass is assumed to be constant.

Suppose the substance  $AB$  is a liquid at the temperature in question;  $CD$  and  $AD$ , solids; and  $BC$  a gas. Further, we will assume the use of an excess of  $AB$  as solvent, and consider the above equation as applied to the reaction taking place in this liquid medium.

Then  $C_{AB}$ , being very great in comparison to the other concentrations, will not change appreciably during the course of the reaction in either direction;  $C_{CD}$  represents the concentration of (solid)  $CD$  dissolved in  $AB$ ,  $C_{AD}$  the concentration of (solid)  $AD$  dissolved in  $AB$ , and  $C_{BC}$  the concentration of gaseous  $BC$  dissolved in  $AB$ . The latter concentration — gaseous  $BC$  dissolved in  $AB$  — is maintained by the pressure, or enforced concentration of the gas in the closed space above the liquid.

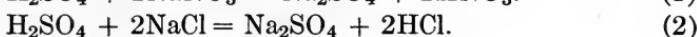
If, now, the mixture is opened to the air, there is nothing to prevent the gas from escaping. It leaves the liquid, as well as the open space above, since the former cannot hold as much under the diminished pressure of gas above.

Turning to the relation  $\frac{C_{AD} \times C_{BC}}{C_{AB} \times C_{CD}} = K$ , we see that to restore

the quotient to its constant value after  $C_{BC}$  has been diminished, it is necessary for  $C_{AD}$  to increase, or  $C_{AB} \times C_{CD}$  to diminish. Readjustment along these lines is accomplished by reaction between  $AB$  and  $CD$  to form  $AD$  and  $BC$  anew. But, the formation of more  $BC$  is attended by its further escape, so that equilibrium is again disturbed; the same process again ensues, and becomes progressive as long as both  $AB$  and  $CD$  remain in the mixture.

The action of sulphuric acid on salts of less volatile acids may be cited as a very common reversible change which results in continuous formation of the volatile substance — in this case, the less volatile acid — unless checked by a retaining (closed) vessel.

Thus, *nitric acid* and *hydrochloric acid* are made commercially by treating their salts with *concentrated sulphuric acid*:



Applying the mass action principle — for equilibrium:

$$(1) \frac{C_{\text{Na}_2\text{SO}_4} \times C^2_{\text{HNO}_3}}{C_{\text{H}_2\text{SO}_4} \times C^2_{\text{NaNO}_3}} = K, \text{ and } (2) \frac{C_{\text{Na}_2\text{SO}_4} \times C^2_{\text{HCl}}}{C_{\text{H}_2\text{SO}_4} \times C^2_{\text{NaCl}}} = K_1.$$

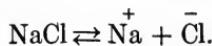
In (1) or (2) the second term of the numerator becomes smaller when the equilibrium mixture is opened, owing to escape of *nitric acid* or *hydrochloric acid* respectively. *Nitric acid* is a liquid at ordinary temperature and pressure, but very volatile at a temperature which causes no appreciable volatilization of *sulphuric acid*, also a liquid. *Hydrochloric acid* is a gas under ordinary conditions. The other materials are solids, non-volatile, except at high temperatures.

As explained above, these reactions will proceed towards the right in a continuous attempt to restore equilibrium — by increasing the numerator product and decreasing the denominator product; always ineffectual, however, owing to the escape of one component material as soon as it is formed.

Towards the close of Chapter VII (on page 87 and succeeding pages) it was pointed out that precipitation occurs on mixing aqueous solutions of different acids, bases, or salts, when such mixture brings appreciable concentrations of certain ions into

the presence of one another. Application of the *Mass Action Law* to the electrolytic dissociation of these substances leads us to a clearer perception of precipitation phenomena.

According to this law, **equilibrium between any electrolyte and its ions** is defined in terms of the several concentrations involved, i.e., those of the undissociated substance, and of the different ions. For example, an aqueous solution of *sodium chloride* contains *undissociated salt*, *sodium ions* and *chloride ions* in such proportions that a certain definite and characteristic value is reached by the expression  $\frac{C_{Na}^+ \times C_{Cl}^-}{C_{NaCl}}$  corresponding to the reversible action:



$$\text{That is, } \frac{C_{Na}^+ \times C_{Cl}^-}{C_{NaCl}} = K,$$

and  $K$ , the equilibrium coefficient, in such a case, may be more appropriately termed, the **dissociation coefficient**.

If the solution contains as much *sodium chloride* as will dissolve at the given temperature, i.e., if it is saturated, the term  $C_{NaCl}$  possesses a constant value, and the above expression reduces to,

$$\frac{C_{Na}^+ \times C_{Cl}^-}{\text{const.}} = K,$$

which may be re-formed thus,

$$C_{Na}^+ \times C_{Cl}^- = k,$$

where  $k$  represents a third constant called the **solubility product**.

A **saturated solution of sodium chloride** must, then, contain ions in sufficient quantity so that the product of their concentrations equals a certain definite value. If additional ions (of the same kinds) were introduced, in some way, they would be forced to combine, and the resulting *sodium chloride* would precipitate, since the solution can hold no more of it.

A **substance, which is commonly called insoluble**, produces very few ions when placed in water. That is, its solubility product is small. If highly dissociated soluble substances, which

together yield the pair of ions corresponding to this insoluble substance, are dissolved in water and poured together, a **precipitate** will result, because the solubility product of the latter substance is sure to be exceeded at once.

If a substance yielding *sodium* or *chloride* ions is dissolved in a saturated solution of *sodium chloride*, precipitation of the latter is caused. This illustrates the **common ion effect**, which may be understood in its general aspect by noting the following explanation of the case in point.

Suppose *sodium nitrate* is dissolved in a *saturated solution of sodium chloride*. The relation  $C_{\text{Na}}^+ \times C_{\text{Cl}}^- = k$  which especially characterizes this latter solution, will, then, be disturbed by the increase in the concentration of *sodium ions* following solution of the former salt. To restore the product to its normal value, *sodium ions* will unite with *chloride ions* to form *undissociated sodium chloride*. In other words, the reaction (page 103) will proceed towards the left. Since the solution is already saturated, any *undissociated sodium chloride* formed in this way cannot remain in solution, but must precipitate. *Potassium chloride* would produce the same effect by increasing the concentration of the *chloride ions*. Substances giving no common ion would dissolve in the *saturated solution of sodium chloride* as though no *sodium chloride* were present.

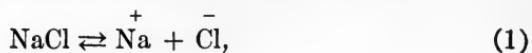
Thus far, in describing the interaction between ions in an aqueous medium, we have taken no account of the presence of *hydrogen* and *hydroxyl ions* from the **dissociation of water itself**. The extremely slight dissociation of water was, however, mentioned in the previous chapter (page 84). If we are dealing with a substance which, when brought under the influence of "water ions"—when dissolved in water—could give rise to a product by the ordinary "crosswise recombination" between ions of the substance and the ions from water, *itself slightly dissociated in measure comparable with that of water*, then the dissociation of water acquires some significance. Since water gives *hydrogen* and *hydroxyl ions*, only *salts* are in a position to produce new undissociated substances by interaction with water, and these new substances must be *acids* or *bases*.

Now, there is a great difference in the degree to which different acids and bases are dissociated (cf. pages 82 and 83), and certain

of them — very weak ones — are so little dissociated that the above effect becomes noticeable when one of their salts is dissolved in water. This type of chemical action involving water is called **hydrolysis**.

To supplement the above statements by a more detailed argument, let us start with a dilute solution of *sodium chloride* in pure water:

The primary reaction involved is,



such that,

$$\frac{\text{C}_{\text{Na}}^+ \times \text{C}_{\text{Cl}}^-}{\text{C}_{\text{NaCl}}} = K.$$

To describe the dissociation of water we write,



and,

$$\frac{\text{C}_{\text{H}}^+ \times \text{C}_{\text{OH}}^-}{\text{C}_{\text{H}_2\text{O}}} = K_2.$$

For the crosswise reactions:



the relations:

$$\frac{\text{C}_{\text{H}}^+ \times \text{C}_{\text{Cl}}^-}{\text{C}_{\text{HCl}}} = K_3, \text{ and, } \frac{\text{C}_{\text{Na}}^+ \times \text{C}_{\text{OH}}^-}{\text{C}_{\text{NaOH}}} = K_4,$$

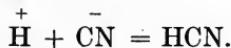
must obtain.

Now, the dissociation coefficient  $K$  of *sodium chloride*, a salt, is large, that is, in the expression following equation (1), the terms  $\text{C}_{\text{Na}}^+$  and  $\text{C}_{\text{Cl}}^-$  are large, while the term  $\text{C}_{\text{NaCl}}$  is small. On the other hand, the coefficient for *water*  $K_2$  is extremely small, or the terms  $\text{C}_{\text{H}}^+$  and  $\text{C}_{\text{OH}}^-$  in the expression following equation (2) are extremely small.

Consider to what extent *undissociated hydrochloric acid* or *undissociated sodium hydroxide* would be formed by the union of their ions — present as specified above — until the relations following equations (3) and (4) are satisfied. Both of these substances are highly dissociated — HCl a strong acid and NaOH

a strong base — therefore the coefficients  $K_3$  and  $K_4$  will be large. On comparing the equilibrium relations corresponding to reactions (1) and (3), bearing in mind that the two expressions  $\frac{C_{Na}^+ \times C_{Cl}^-}{C_{NaCl}}$  and  $\frac{C_H^+ \times C_{Cl}^-}{C_{HCl}}$  are not far different in value, and that  $C_{Cl}^-$  is the same in both, we see that, since  $C_{NaCl}$  is small in the first expression where  $C_{Na}^+$  is large, the corresponding term  $C_{HCl}$  in the second expression, where  $C_H^+$  is extremely small, must possess a trifling value. The same conclusion regarding the concentration of *undissociated sodium hydroxide* follows from a comparison of the equilibrium relations corresponding to reactions (1) and (4). Thus, no appreciable quantities of *hydrochloric acid* or *sodium hydroxide* are formed by hydrolysis when *sodium chloride* is dissolved in water.

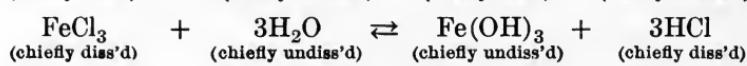
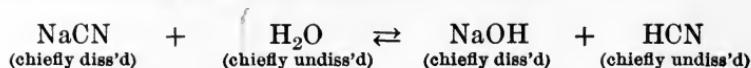
If, however, we replace the strong acid HCl by a very **weak acid**, for example, HCN, the corresponding salt NaCN will be largely dissociated, as was NaCl. But this acid is very slightly dissociated — comparable to water — and the expression  $\frac{C_H^+ \times C_{CN}^-}{C_{HCN}}$  must reach a very small value to represent equilibrium between the acid and its ionization products. The numerator product  $C_H^+ \times C_{CN}^-$  even though  $C_H^+$  is very small, will here be much larger than this equilibrium value, and a considerable amount of undissociated HCN will be formed, according to the reaction:



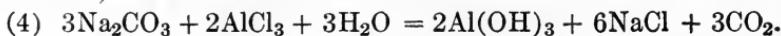
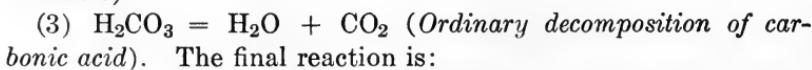
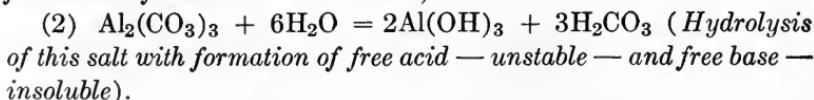
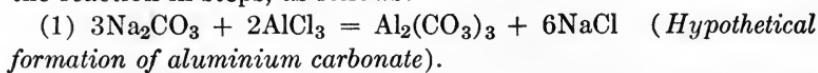
As *hydrogen ions* are used up in this change, the equilibrium between *water* and its ions is disturbed and more *water* will dissociate — reaction (2) will proceed towards the right — until complete readjustment is effected. This production of additional *hydrogen ions* is, of course, accompanied by an equivalent production of *hydroxyl ions*, which have no tendency to unite with *sodium ions*, as we have previously noted. Hence, they accumulate in the solution giving it alkaline properties.

When the salt corresponds to a **weak base and a strong acid**, hydrolysis occurs, and is explained in the same general way as above. In such a case, undissociated base is formed and the solution possesses acid properties.

The following reactions illustrate both cases:



If both acid and base are very weak, hydrolysis of the corresponding salt may be so nearly complete that the latter cannot exist appreciably in the presence of water. Sulphides and carbonates of aluminium, chromium, and iron ( $\text{Fe}^{+++}$ ), are, thus, stable only in the dry state. When reagents, calculated to form one of these substances, are mixed, the products of its hydrolysis result instead. For example, the addition of sodium carbonate to aluminium chloride, in solution, causes precipitation of aluminium hydroxide, and evolution of carbon dioxide. We may write the reaction in steps, as follows:



## CHAPTER IX.

### HETEROGENEOUS EQUILIBRIUM.

ANY single variety of material may assume a number of different physical forms, according to the physical influences which are brought to bear upon it. The three most apparent differences in this respect are defined by the terms, gas, liquid, and solid. Solid material, in particular, is subject to further classification, as previously noted (Introduction, page 16), whereby we speak of amorphous, or specific crystalline modifications. When different substances are brought into close association with one another, the matter occurring in any one of these three forms may consist of mixed material, each respective form being homogeneous in its own makeup and presenting the same general appearance as if pertaining to a simple substance. Thus, we are familiar with mixed gases or liquids, and somewhat less so with mixed solids, in the sense that they are completely "dissolved" in one another (cf. Introduction, pages 4 and 20). On the other hand, it is not necessary that the liquid corresponding to one kind of material, should completely mix with that corresponding to another kind of material, when both are placed in contact. The two liquids may remain in contact with one another, separated by their own surfaces (cf. Introduction, page 20). Two different solids most frequently fail to mix, except mechanically, when rubbed together. Gases invariably merge into one another. Thus, we see that a system of associated material may consist of several separately homogeneous fractions in mechanical contact.

These individual physical modifications comprising the system are called **phases**.

The different chemical substances taken at will to produce a collection of *phases*, are called **components**.

The nature of the phases appearing in a given system, as well

as the number of phases which may remain in contact without tendency to alteration, is primarily dependent on the physical conditions, i.e., temperature, pressure, and concentration (of the several components), under which the system is required to exist. For example, it is the solid form of iodine which we handle in the laboratory, because this is the stable form under ordinary conditions. If we elevate the temperature of this solid substance at atmospheric pressure, it changes into vapor, i.e., it sublimes, when a certain temperature is reached, because, at this point, the latter form becomes capable of existence, and is, therefore, formed when heat is added to the solid. If, when part of the solid is transformed into vapor, the heating is made merely sufficient to keep the temperature constant — to prevent subsequent cooling — both solid and vapor will continue to coexist. Had we increased the pressure sufficiently before heating the solid, liquid, instead of vapor, would have resulted — the solid iodine would have melted.

When a number of substances are placed in contact, great variety in the configuration of the system is possible, as the temperature, pressure, and concentrations are altered. Owing to the discovery by Gibbs (Yale, 1874–8), of a simple numerical relation between the number of **phases**, the number of **components**, and the number of **physical conditions which may be varied independently of one another** within certain limits without causing the disappearance of any current phase, or the appearance of any new phase, — in any system, chemical or physical — we are in a position to impose a well ordered classification upon what at first appears to be a bewildering diversity of equilibrium phenomena.

Denoting the number of variable conditions, in the above connection, by  $V$ , the number of components by  $C$  and the number of phases by  $P$ , we have, according to **Gibbs' Phase Rule**,

$$V = C + 2 - P,$$

or, in words, *When the different phases, composing a given system, are in a state of equilibrium, the number of physical conditions which may be independently varied without disturbing this equilibrium, is equal to the number of components increased by 2, less the number of phases.*

The following special cases may be noted:

(1) If the system shows two more phases than components, no one of the obtaining conditions may be varied without subjecting the whole system to readjustment resulting in a different number of phases ( $C - P = -2$ , and  $V = 0$ ). The system is then said to be *nonvariant*.

(2) If the system shows one more phase than components, one condition may be varied at will — to a certain limited extent — without disturbing the equilibrium ( $C - P = -1$ , and  $V = 1$ ). The system is *monovariant*.

(3) If the system shows the same number of components as phases, two conditions may be varied independently without disturbing the equilibrium ( $C - P = 0$ , and  $V = 2$ ). The system is *divariant*.

In a phase system generated from a single component, the variable conditions are the temperature and the pressure. When two components replace the one, there obtains the additional factor of concentration, which may be varied at will, thereby constituting a third variable condition.

A simple one-component system, in which equilibrium is determined by the temperature and pressure alone, will be chosen, on account of simplicity, to illustrate the general application of the phase rule. The disposition of each of the three possible phases, gaseous, liquid, and solid (leaving out the possibility of more than one solid phase) with respect to the pressure and temperature, may be represented graphically on a plane surface. We have already made use of such a pressure — temperature diagram (page 51) — to represent the different vapor tensions of a solid corresponding to different temperatures (sublimation curve of the solid), as well as the different vapor tensions of a liquid corresponding to different temperatures (vaporization curve of the liquid). In the accompanying diagram (Fig. 7), similar curves, numbered 1 and 2, are drawn. Any point on the sublimation curve — 1, represents a temperature and pressure at which solid and vapor can coexist, i.e., are in equilibrium. Any point on the vaporization curve represents a temperature and pressure at which liquid and vapor can coexist. The point where both curves meet represents the temperature and pressure at which solid, liquid, and vapor can coexist (cf. Chapter III,

page 52). Solid and liquid, which are in equilibrium (with vapor) at  $O$ , continue in equilibrium when the temperature and pressure are altered, as shown by the curve numbered 3 which meets curves 1 and 2 at  $O$ . In other words, this curve indicates the change in the melting point of the substance with the pressure.

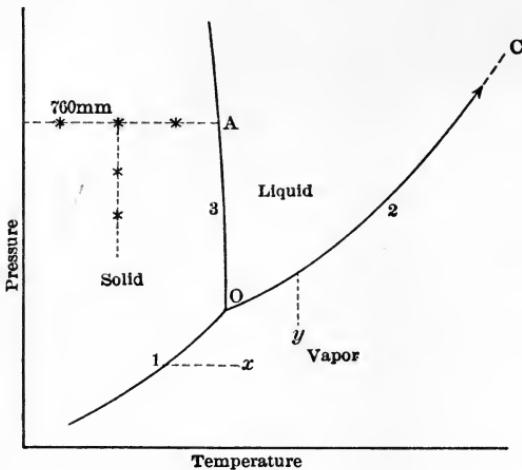


Fig. 7.

As drawn in the diagram, it corresponds to a decrease in melting point with an increase in pressure, a condition illustrated by the familiar solid phase of water, namely, ice.

Consider the physical change which occurs when we pass from any point on the sublimation curve directly towards the right, i.e., increase the temperature at constant pressure. Solid and vapor, which are in equilibrium at the temperature and pressure corresponding to this point, will no longer continue to coexist, but the solid will become completely transformed into the vapor. That is, the temperature cannot rise until the solid has absorbed heat enough to convert it into vapor. In like manner, passing from a point on the vaporization curve directly towards the temperature axis, i.e., decreasing the pressure at constant temperature, we note a disappearance of the liquid phase, corresponding to complete change of the material into vapor. The points  $x$  and  $y$  with attached dotted lines, serve to suggest the above changes. It should be clear that the whole field in which

these points are situated, bounded by curves 1 and 2, represents concurrent temperature and pressure values, at which the substance must exist completely in the form of vapor. This field is, therefore, defined on the diagram by the word, **Vapor**. The remaining space is divided between a **Liquid** field, bounded by curves 2 and 3, and a **Solid** field, bounded by curves 1 and 3. In passing from one field to another across a boundary line, discontinuity occurs — there is a time when both phases are in contact. It is, however, possible to pass around the vaporization curve (2) from the vapor field into the liquid field, or *vice versa*, by suitably altering the temperature and pressure, since this curve possesses a determinate end point. There would be no discontinuity in such transformation. The end point *C* is called the **critical point**. We have already noted the existence of a **critical temperature**, above which, no matter how great the compression, the vapor cannot be converted into liquid. In other words, liquid does not exist above this temperature, and the vaporization curve (giving its vapor tension) must end here. At the point *C*, then, we have reached the critical temperature and pressure of the liquid.

The diagram which we have discussed above may be regarded as a map showing the configuration of a one component system, with respect to the temperature and pressure. The fundamental curves 1, 2, and 3 are determined by experiment. Hence we have here an arrangement of experimental results, which should be of assistance in the interpretation of the phase rule.

Referring again to the diagram, it is clear that, in any one of the three fields, solid, liquid, or vapor, a great variety of temperature and pressure values may be chosen quite independently of one another to represent the conditions under which the corresponding phase is existent. To make the illustration concrete, ice, at atmospheric pressure, may be subjected to a number of different temperatures (limited by its melting point) without sustaining any physical change. Stars on the upper dotted line in the diagram, represent such different temperatures. At any of these temperatures, for example that represented by the second star, the pressure may be diminished at will — indicated by the perpendicular dotted line with stars — provided it does not fall below the sublimation pressure at this temperature, without

causing the solid phase to change. Thus, on experimental grounds, we conclude that the one component system, embracing a single phase, is divariant.

According to the phase rule, such a system should be divariant. For,  $C = 1$ , and  $P = 1$ . Whence,  $V = 1 + 2 - 1$ , or 2.

It has been pointed out that each of the curves 1, 2, and 3 defines the temperatures and pressures under which a certain pair of phases may coexist. The temperature corresponding to a point on one of these curves may be altered without causing either phase to disappear, provided the pressure sustains a perfectly definite alteration at the same time, whereby a new point on the same curve results. In order that the same equilibrium continue, variation of one condition must be accompanied by (dependent) variation of the other condition. Both may not be varied independently. Since only one condition at a time may be varied arbitrarily, the equilibrium is termed monovariant. Turning again to the system —  $\text{H}_2\text{O}$  for a concrete illustration, we note that the point  $A$  on curve 3 corresponds to the melting temperature of ice under atmospheric pressure. At this temperature  $0^\circ \text{ C}$ . and under atmospheric pressure, ice and liquid water are in equilibrium. Both phases remain in equilibrium at temperature-pressure values along the curve  $AO$ . Thus, on decreasing the pressure from 760 mm. ( $A$ ) to about 4 mm. ( $O$ ), a temperature slightly less than  $0.01^\circ$  above  $0^\circ \text{ C}$ ., must correspond to the latter pressure value, if no change in the equilibrium is to occur. Greater elevation of the temperature at this pressure will bring about complete transformation of solid into vapor, i.e., we pass into the vapor field on leaving the curve at  $O$ , as specified.

The phase rule requires this system to be monovariant, in agreement with the experimental conclusion. For, here,  $C = 1$ , and  $P = 2$ . Whence,  $V = 1 + 2 - 2$ , or 1.

At the point  $O$  all three phases are in equilibrium. This point is called a **triple point**. Obviously, no change of either temperature or pressure is possible without passing into one of the three adjacent fields. The system, in this condition, is, therefore, nonvariant.

In this case, the expression,  $V = C + 2 - P$ , becomes,  $V = 1 + 2 - 3$ , or  $V = 0$ , a result in complete agreement with the above.

We have seen that the coexistence of two or more phases is rendered possible under properly chosen conditions of temperature, pressure and concentration. The general state of coexistence, in this connection, is defined by the expression **heterogeneous equilibrium**. That equilibrium of this sort differs in the degree of its flexibility in the face of changing conditions, has been shown in the last few paragraphs. If the phases concerned are capable of coexisting at one temperature alone when the pressure is arbitrarily chosen, a most complete and satisfactory regulation of their equilibrium must be conceded. The phrase **complete heterogeneous equilibrium** is applied in defining this condition. The equilibrium along each curve in the diagram is complete in this sense. Thus, ice and liquid water are in a condition of complete heterogeneous equilibrium at  $0^{\circ}$ , under 760 mm. pressure; such that any alteration of the temperature or pressure, without corresponding alteration of the pressure or temperature, respectively, is accompanied by the complete disappearance of one phase.

Obviously the phase rule is chiefly important as an instrument for indicating the numerical relation between the number of components and the number of phases, which must characterize this preëminently definite condition of equilibrium. The rule tells us that *complete heterogeneous equilibrium results when the system shows a number of phases which is one greater than the number of components.*

If a relatively smaller number of phases is present, the equilibrium is **incomplete**.

Consider, for example, the system composed of **water vapor and an unsaturated solution of common salt in water**. Here  $C = 2$  ( $H_2O$  and  $NaCl$ ) and  $P = 2$ , or,  $P$  is less than  $C + 1$ . We have seen in Chapter III that solution of salt in water lowers the vapor tension of the latter. At the same temperature, then, unequally concentrated solutions will possess different vapor tensions (cf. Fig. 2, Chapter III, page 51, and discussion). Hence, at a given temperature, many different pressures may correspond to equilibrium between the vapor and liquid phases (the latter possessing definite concentration —  $NaCl$  in  $H_2O$  — for each definite pressure). If, in any specific case, the external pressure is increased, the vapor phase will not completely dis-

appear, but some vapor will be converted into liquid, whereby the solution becomes more dilute, reaching equilibrium with the vapor under another definite pressure. When an excess of salt is added to the solution, the equilibrium becomes complete. There are now three phases, solid NaCl, saturated solution, and water vapor, i.e., one in excess of the number of components. At a given temperature, a single vapor pressure corresponds to the (saturated) solution. If the external pressure is increased, vapor condenses, but the solution cannot become less concentrated, on account of the presence of solid NaCl; therefore no new equilibrium is reached, and the vapor continues to condense until it is no longer present.

The addition of ice to the last mentioned mixture, increases the number of phases to four. According to the phase rule,  $V = 2 + 2 - 4$ , or 0. There will be a single temperature and pressure at which the saturated solution is in equilibrium with solid H<sub>2</sub>O, solid NaCl, and vapor. If the mixture is opened to the air, the latter phase is not concerned in the equilibrium, since vapor may escape freely. Neglecting this phase, then, we have,  $V = 2 + 2 - 3$ , or 1. Under atmospheric pressure, these three phases require a certain definite temperature to determine their coexistence. This temperature is considerably below the freezing temperature of water. If the temperature of the mixture were above this equilibrium value at the outset, ice would melt, thereby absorbing heat, until the proper lowering had resulted. Corresponding to the dilution of the solution due to this process, solid salt would dissolve, keeping the solution saturated. The final state of equilibrium would be maintained without change in the amount of any phase, provided no change in the external conditions were imposed. If, as is frequently the case, such a mixture were used to cool some foreign substance, ice would continue to melt — absorb heat — in the endeavor to maintain the equilibrium temperature within the system.

## CHAPTER X.

### THERMOCHEMISTRY.

It is a matter of common experience that chemical change is accompanied by heat evolution or heat absorption — aside from the recombination of matter on an altered plan, which especially characterises such change, there is a **redistribution** of **energy** effected in such a way that either previously bound (chemical) energy is set free in the form of heat, or available heat energy (supplied from without to carry on the reaction) is appropriated and properly disposed as chemical energy in the new system.

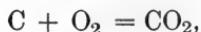
Our ordinary chemical equations do not represent these associated heat changes, but it should be well understood that the quantity of heat evolved or absorbed during any given chemical change, under definite conditions, is quite as specific and definite as is the nature of the substances formed — specified in the equation.

To properly record the heat effect corresponding to any given reaction, we must adopt some system of measuring heat, and then specify certain fixed amounts of the reacting substances. The first of these requirements is realized by referring quantities of heat to a unit quantity, called the **calorie**, sufficient to elevate the temperature of one gram of water one degree centigrade; the second, by uniformly choosing gram molecules of the different substances in the proportions defined by the equation as a basis for the thermal data. In place of the **gram calorie**, defined above, the **kilogram calorie**, or the heat quantity required to elevate 1000 g. of water one degree centigrade, is frequently used as a more convenient measure when the heat effects are considerable. These terms are commonly abbreviated to *cal.* and *Cal.* respectively.

The **direct measurement of a heat effect** attending a given chemical reaction is effected by enclosing the reaction mixture in a suitable vessel, placing the latter in a calorimeter, and then

starting the process, perhaps by an electric spark. The calorimeter is usually a receptacle containing a weighed quantity of water (water calorimeter) which is kept in agitation by a stirring apparatus to insure an even distribution of heat, supplied with an apparatus — thermometer — for measuring the temperature. Heat from the reaction, raises the temperature of the water in the calorimeter, and observation of the temperature difference before and after the reaction, coupled with knowledge of the amount of water involved, enables us to calculate the total heat quantity concerned in changing the temperature of the water. Some heat is used in raising the temperature of the containing vessel. Suppose this vessel is made from some definite kind of material. Then, a well-defined amount of heat will be required to raise the temperature of one gram of this substance one degree. This amount expressed in calories is called the *specific heat* of the material. The weight of the vessel (in grams) multiplied by its specific heat gives the heat quantity required to raise it one degree. This value multiplied by the temperature difference noted above gives the heat quantity used to produce its elevation to the final temperature of the experiment, which must be added to the value calculated from the change in temperature of the water. Other corrections are necessary, according to the general method of procedure.

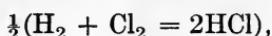
The heat effect accompanying a reaction is called, in general, the **heat of reaction**. Owing to the existence of distinct varieties of chemical action, we may substitute more descriptive terms for this general term. Thus, the student will readily appreciate the logic of designating the heat of reaction when 12 g. of carbon are completely burned to carbon dioxide, according to the equation:



as the **heat of combustion**, or the **heat of oxidation** of carbon. This heat effect is very considerable, amounting to about 100 Cal.

Again, the heat evolved or absorbed when one gram molecule of a compound is formed from its elements, is called its **heat of formation**. If heat is evolved during such formation, the compound or reaction is said to be **exothermic**; if absorbed, the term **endothermic** is applied.

When 1 g. of hydrogen combines with 35.5 g. of chlorine:



about 22 Cal. of heat are liberated. The heat of formation of the exothermic compound, hydrochloric acid, is, therefore, 22 Cal.

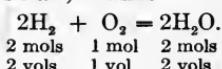
Most compounds are exothermic. As an example of the other, or less common type, we may mention acetylene  $\text{C}_2\text{H}_2$ , one gram molecule of which is formed from its elements under a heat absorption of about 53 Cal. When this endothermic compound is burned, in addition to the heat of combustion due to the carbon and hydrogen which it contains, there is an evolution of 53 Cal. corresponding to the decomposition itself.

The descriptive terms, (latent) **heat of fusion** and (latent) **heat of vaporization**, commonly signify in physics, the heat quantity required to completely melt, or vaporize one gram of the substance at its melting point, or boiling point respectively. Such values must be multiplied by the molecular weights of the substances to which they refer, if they are to be used in a chemical connection.

Obviously, the heat evolved by a given reaction will depend upon the states of aggregation of the substances in general. Thus, the heat of formation of liquid water at  $100^\circ$  is about 68 Cal. Some of this heat, however, will go to vaporize the water, so that in practice, water vapor, instead of liquid water, will be formed. The heat quantity necessary to convert one gram molecule of liquid water at  $100^\circ$  into water vapor, at the same temperature, is about 9.5 Cal. Hence, the difference,  $68 - 9.5$ , or 58.5 Cal. will be evolved when one gram molecule of water vapor is formed. In the above case, passing directly from the gases, hydrogen and oxygen to water vapor, at the constant temperature,  $100^\circ$ , we have a heat evolution of 58.5 Cal.:



\* In order that the equation may show one molecule of water, atoms instead of molecules of hydrogen are represented. In general, equations should show **molecules**, when the volume relations (in the case of gases) are at once apparent (by Avogadro's Law). Thus:

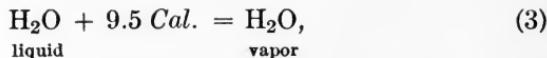


Cf. pages 14 and 28.

Considering this as a dual process:



and,



we obtain by summation,  $58.5 \text{ Cal.}$  ( $68 + - 9.5$ ), the final heat effect to be written as a positive value in the right hand member of equation (1).

In this way, we may pass from one system to another through many individual physical and chemical processes, or directly in one operation, but the final heat effect representing the sum of all heat effects concerned in the entire series of constituent changes, will invariably be the same. This principle known as the **Law of Hess**, may be concisely stated as follows:

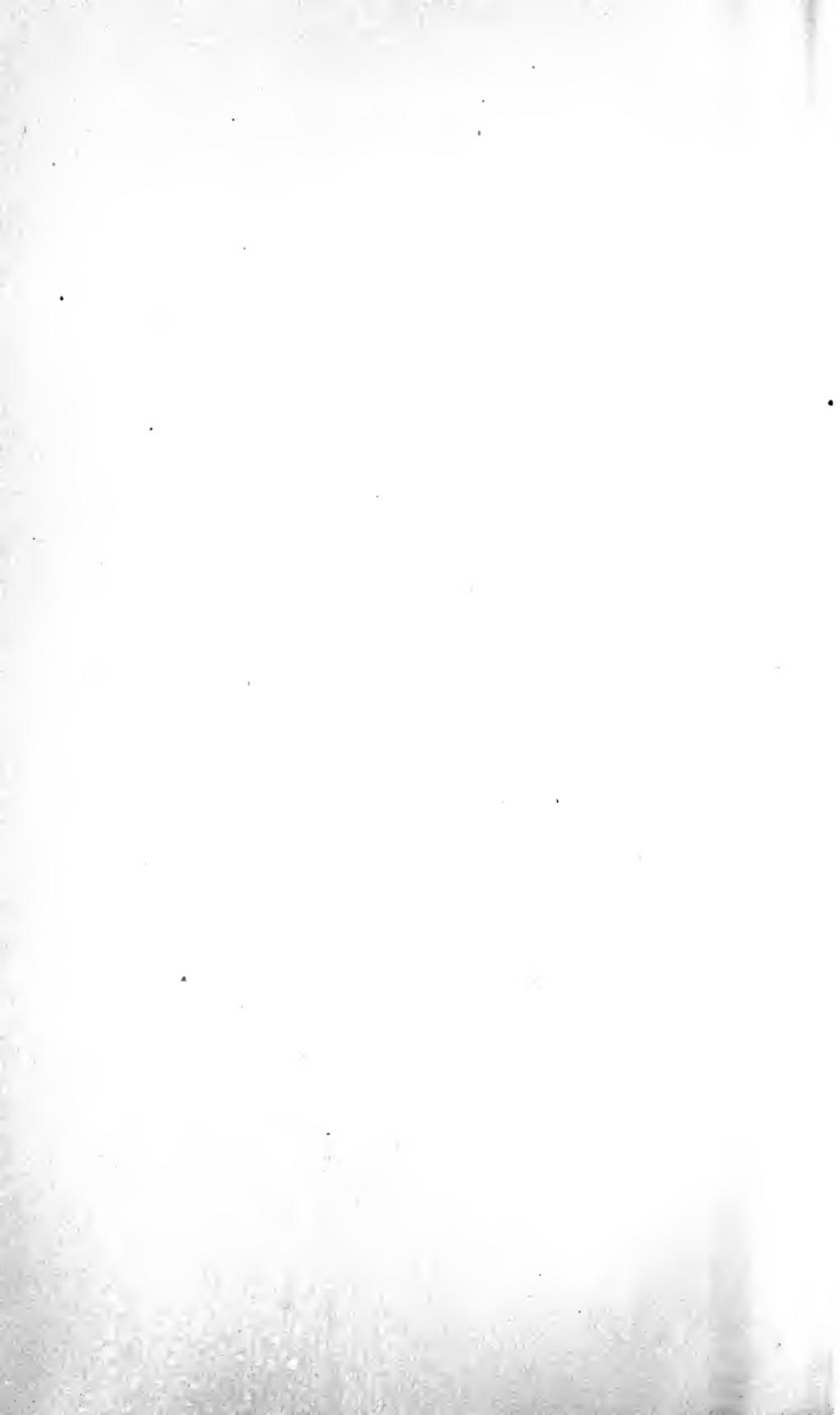
*The total calorific effect which accompanies the transformation of one chemical system into another is independent of the steps passed through.*

The thermal behavior of acids, bases, and salts in aqueous solution was not well understood until the advent of the electrolytic dissociation theory. When solutions of electrolytes in the dissociated condition are mixed and no marked combination between the ions occurs, there will be no marked heat effect. Thus, we refer to the *thermo-neutrality* of salt solutions. Since salts are dissociated to the same general extent, which we may regard as practically complete in ordinarily dilute solution, no appreciable change takes place when dilute solutions of different salts are mixed. When a salt is dissolved in water, there is a heat effect, corresponding to the dissociation of its molecules into ions.

The reaction which alone occurs to any extent when a dilute solution of any strong acid is mixed with a dilute solution of any strong base, is:



Hence, the same heat effect accompanies all **neutralization reactions** in dilute solution, where strong acids and bases are concerned.



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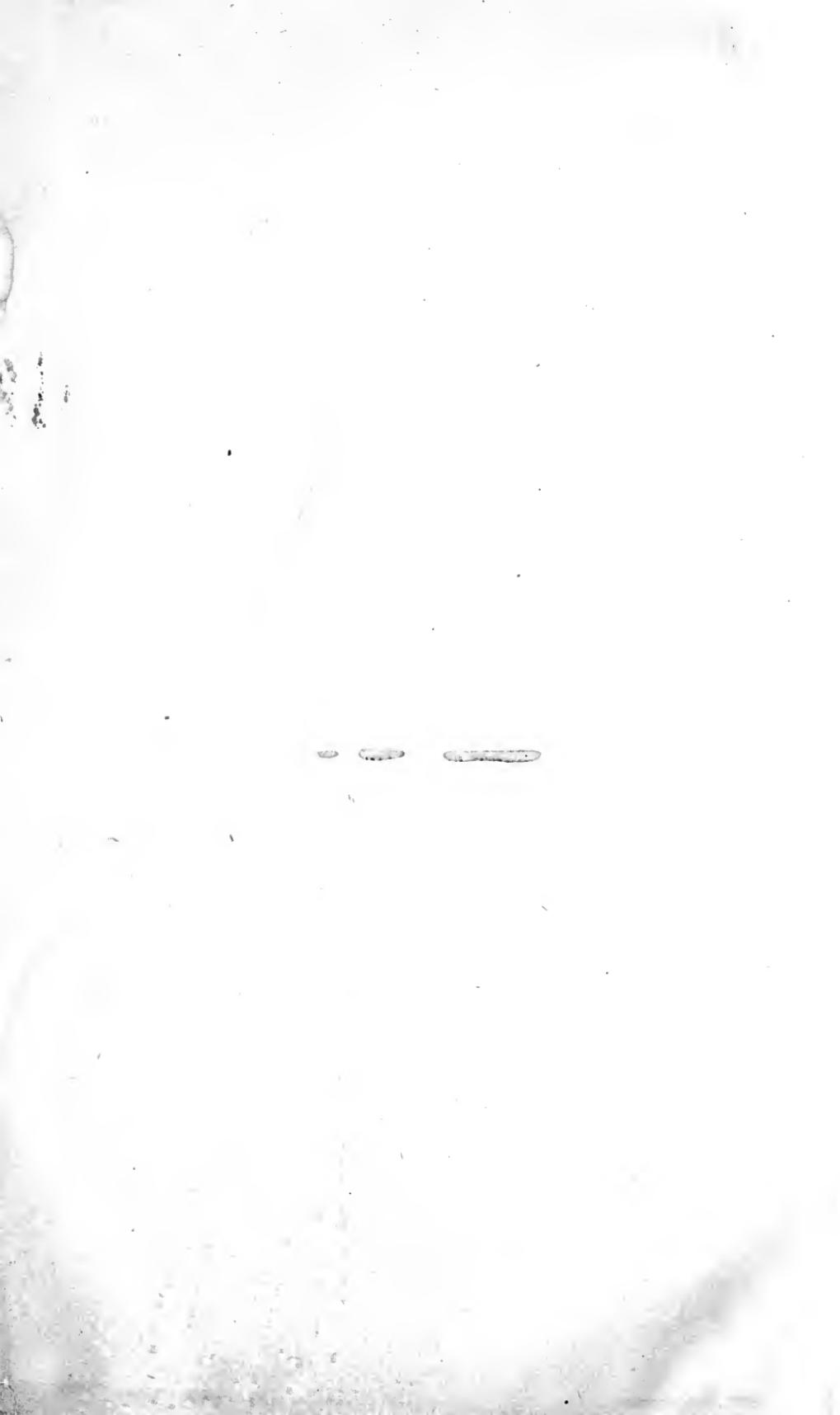
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